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Energy
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Emerging Environmental Technologies

An Analysis of New Treatment Technologies for the California Energy Commission

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REPORT SUMMARY

As the state's principal agency dedicated to energy policy and planning, the California Energy Commission is charged with the responsibility to develop energy technologies and promote energy efficiency. This report describes an effort by EPRI to identify emerging electric-based environmental treatment technologies on which the Commission should focus research efforts.

Background

As environmental consciousness grows, the public demands more effective environmental treatment methods. New, more advanced and energy-intensive technologies will be a key component of meeting the higher level of quality now demanded. A plethora of new electrotechnologies under development shows significant promise. However, it is difficult to judge the most promising ones. For the purposes of this report, electrotechnologies were defined as environmental treatment processes that use electricity to effect physical, chemical, or biological changes in air, water, or solids. This study was conducted to identify those electrotechnologies on which the Energy Commission should focus research efforts.

Objectives

- To pursue development of energy technologies in an efficient and justifiable manner.
- To identify the most promising, emerging treatment technologies.
- To provide the Commission with guidelines on appropriate methods for further technology development.

Approach

The project team conducted a literature search to identify over forty treatment technologies. Technologies ranged from the mundane and standard approach of biological treatment to more exotic and experimental methods such as electrohydraulic cavitation. The team used a two-stage evaluation process to identify the most promising ones. The first stage simply assessed if the technology used energy and whether the technology had achieved commercial status. If both answers were affirmative, the technology was passed through a second, more quantitative evaluation. The quantitative evaluation considered a number of criteria for the technology, including its status, range of potential applications, interest from other researchers, importance to problems of concern in California, and its potential competitiveness.

Results

The evaluation process yielded eight technologies considered to be very promising. These technologies were studied in further detail to assess the theory, current research status, and developmental needs of each one. Based on this assessment, recommendations for Commission action are included.

EPRI Perspective

As the principal research organization in the U.S. energy industry, EPRI is dedicated to improving the environment in a sustainable manner. Environmental treatment processes must continue to evolve to meet the more stringent demands of the public. These processes will require the use of energy to achieve these higher levels of treatment.

The technologies presented in this study show tremendous potential, but all require additional research and development to reach commercial status. Electric utilities can play a key role in this development by working with their important industrial customers to identify and demonstrate promising applications.

Keywords

Emerging technologies
Electrodewatering
Dielectric heating
Nonthermal plasma technology
Freeze conditioning
Supercritical water oxidation

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1
INTRODUCTION

Numerous electricity-based treatment processes, or electrotechnologies, are available to U.S. industry to address a variety of environmental problems, including wastewater treatment and air pollution control. Some, such as microfiltration and ozonation, are well established and commercially available. Others, such as radiofrequency (RF) drying and electron beam irradiation, are more experimental. Further development is necessary to bring these technologies to market. It is thus important to develop an understanding of the current and future performance and cost of electrotechnologies for environmental protection purposes.

The objective of this study was to identify emerging electrotechnologies holding potential for providing solutions to a variety of environmental issues facing the United States, and in particular, California. For the purposes of this report, electrotechnologies were defined as environmental treatment processes that use electricity to effect physical, chemical or biological changes in air, water or solids. This assessment describes the technical and economic status of emerging electrotechnologies, identifies constraints on these electrotechnologies reaching market status, offers projections for their future performance and costs, and includes key vendors of these technologies. The resulting report will allow the California Energy Commission (CEC) to effectively target future research into improving the economic and public benefits of electrotechnologies.

One mission of the California Energy Commission is to conduct research into innovative methods of pollution control. Given the speed at which innovation can occur today in the pollution control field, there are a large number of technologies now under development which show promise to reduce costs, improve the environment, and are worthy of further research and development. Given finite resources, these many options must be prioritized to determine the most appropriate ones for additional funding. This document is a summary of efforts to prioritize emerging environmental technologies.

A three-step process was used to identify, assess and characterize emerging technologies. The first step involved the development of an exhaustive list of emerging treatment technologies to clean air, water, hazardous waste and solid waste. Once the list was established, each technology was briefly assessed to determine its commercial availability (i.e. was it emerging or established) and whether it used energy. If the technology was an emerging technology that used energy, it passed to the second step for more careful consideration. This first step was also used to classify and consolidate a technology that may be referred to by different names in the literature.

The second step, conducted on those technologies that were accepted for screening, involved developing a brief description of the technology and assessing it based on five criteria, including breadth of potential applications, potential for collaborative funding from other entities, the technology status, and the impact of the technology on California industry. These criteria are discussed in more detail in Chapter 3.

The criteria were used in a rating system to determine the most promising technologies. A detailed analysis of the 'state-of-the-art' was conducted on the most promising technologies. The detailed analysis of the chosen technologies begins in Chapter 4. Each technology has its own section within that chapter. These include electrodewatering, dielectric heating, capacitive deionization, supercritical water oxidation, an innovative advanced oxidation process, freeze conditioning, and non-thermal plasma technologies.

The report details recent advances and the research challenges facing the chosen electro-technologies that in the future may be used in a variety of environmental applications. Each description includes the theory behind the technology, a summary of past efforts, anticipated costs, and recommendations to the California Energy Commission on appropriate research needs. With judicious use of research money, a significant impact could be made to the environmental marketplace.

2
INITIAL SCREENING OF TECHNOLOGIES

The first step in the study required a perusal of the literature to list existing and potential electrotechnologies. This first effort yielded forty to fifty different technologies with potential applications in the environmental marketplace. It was immediately recognized that such a large number of technologies is too unwieldy, so an initial screening tool was devised and used to limit the number to be evaluated. This chapter lists the identified technologies, presents a brief description of each, describes the simple screening process, and the outcome of applying that process to each identified technology.

Generalized List of Technologies

Approximately forty different emerging technologies were identified that have environmental uses. It was the initial goal of the study to gather an exhaustive list of electrotechnologies that have or may have environmental applications. This section summarizes a comprehensive list of electrotechnologies, includes a brief description of each, and provides a short reason behind why or why not the technology is considered further.

A comprehensive list of potential technologies is presented alphabetically in Table 2-1. Before discussing the various technologies, a few short caveats are in order. The principal problem encountered in composing a comprehensive list of any sort is in organizing the list in a coherent fashion. A wide variety of sources were used to develop this list. Grouping technologies under different headings required some arbitrary decisions. Further, different researchers use different terminology to describe the same process. Thus, while every effort was made to include different terms used for these processes, it is possible, in fact likely, that some were missed. Further, many technologies are subsets of others. For instance, ultrafiltration is one type of membrane filtration, and photocatalysis is principally used in environmental applications as an advanced oxidation process. Thus, distinct treatment technologies are listed either by themselves or under a general heading.

Table 2-1
Potential and Existing Environmental Treatment Technologies

• Acoustic sensor for assessing membrane integrity
• Activated carbon absorption & electrical regeneration
  - UV + ozone
  - UV + H_2O_2
  • Photocatalysis
  - UV + TiO_2
  - Nb-doped TiO_2 electrodes
• Advanced oxidation processes
  • Ozone at elevated pH
  • Ozone + hydrogen peroxide
  • Photooxidation
• Air flotation
• Biological treatment
• Capacitive deionization
• Dielectric heating system
  • Microwave systems
  • Radio frequency (RF) systems
• Electrodewatering
• Electrodialysis
• Electrohydraulic cavitation
  • Spark-gap discharge (lithotripsy)
  • Ultrasonic irradiation (sonolysis)
• Electrolysis
  • Electrocoagulation
  • Cerium-catalyzed oxidation process
  • Electrokinetic remediation of groundwater
• Electron beam irradiation
• Electromagnetic leak detection
• Electroosmosis dewatering
• Electrophoresis
• Electrostatic precipitation
	• Enhanced gravity separation
	• Freeze concentration/crystallization
	• Heat pump evaporation
	• High temperature plasma-arc heater/furnace
	• Ion Exchange
	  • Selective ion exchange
	• Incineration
	  • Molten glass incinerator
	  • High-temperature fluid wall reactor
	  • Infrared incinerator
	  • Induction incinerator
	  • Pyrolytic incinerator
	• Infrared drying
	• Low temperature (non thermal) plasmas
	• Mechanical vapor recompression
	• Membrane separation
	  • Geotextile membranes
	  • “Smart” membranes
	  • Microfiltration
	  • Ultrafiltration
	  • Reverse osmosis
	  • ‘Smart’ membranes
	• Photocatalytic oxidation
	• Phytoremediation
	  • Wetlands
	• Ozonation
	• Pyrolysis
	• Supercritical water oxidation
	• Ultraviolet radiation
	• Vacuum pyrolysis
	• Wet air oxidation

Initial Screening of All Technologies

An initial screening was made of all technologies listed in Table 2-1 to determine which of these deserved a closer look. The brief screening, which considered only if the technology used energy and had not yet attained commercially viable status, is summarized below. If the technology used energy and was not commercially viable, a more in-depth analysis was conducted, the results of

which are summarized in Chapter 3. The reasoning behind this review was simple. The purpose of this study is to identify technologies which, with additional research funding, are likely to become commercially viable. If a technology is already viable, it is assumed that additional research funding for development was not needed. It should be noted that while many of these technologies are commercially available, they are not yet commercially viable. In many cases, the purchase of a system not commercially-viable amounts to conducting a demonstration of the process. In the following paragraphs, each technology is listed in **bold** along with a short discussion on why or why not it was considered for a more detailed review.

Acoustic sensor for assessing membrane integrity. Microscopic tears in membranes are the principal cause of membrane failure, but these tears are nearly impossible to find using conventional methods. A French water company is currently developing a sensor which uses sonar to assess the integrity of membrane. This technology is principally for support of a commercially-viable technology, so it was not considered in Chapter 3.

Activated carbon absorption & electrical regeneration. Activated carbon absorption has been used in environmental treatment since before World War II and is a well-established industry. Conventionally, contaminated activated carbon is regenerated in a furnace, where the heat volatilizes the pollutants from the carbon. However, an innovative regeneration technology using electricity could greatly reduce the costs associated with regeneration, so the technique is considered in Chapter 3.

Advanced oxidation processes. Advanced oxidation processes, or AOPs, found widespread use in waste treatment during the 1990s. AOPs encompass a wide range of techniques, but share the trait that they all generate hydroxyl radicals at ambient temperatures and pressures to effect oxidation reactions. Systems based on processes using ozone, UV, and hydrogen peroxide are well established and, in most cases, commercially available. However, there are two innovative systems using a catalyst and electrodes to generate hydroxyl radicals. Thus, while AOPs using ozone, UV and hydrogen peroxide were eliminated from additional study, two new AOPs, one using electrodes doped with elemental niobium and one using electrodes doped with elemental cerium, are assessed in Chapter 3.

Air flotation. Air flotation is a common separation process, particularly in industrial wastewater treatment. Several vendors manufacture and market air flotation equipment to the environmental market, so this process is not a good candidate for further study. However, a new system promises more efficient separation. This improved system is considered in Chapter 3.

Capacitive deionization. Capacitive deionization is an emerging technology that uses the principles of electrodialysis with carbon fiber to remove dissolved solids from water sources. Preliminary results from bench tests suggest that this technology can be effective at desalting water with total dissolved solid concentrations of 5,000 mg/L and higher. Given the process' promising future, it is considered further in Chapter 3.

Dielectric heating systems. In the dielectric heating process, an alternating electric field of high frequency is used to generate heat in non-conductive or dielectric materials, such as water. Both radio frequencies (RF) and microwave frequencies are used. Microwaves are used commercially in many industrial applications, such as curing rubber and in drying various coatings, but have been applied only sparingly to environmental problems. There are a broad

range of possible environmental applications with these promising technologies, but much additional study is needed. Thus, this technology was considered for further study.

Electrodewatering. This process uses direct current to apply an electric charge to the sludge being dewatered in a belt filter press, which is a very common piece of equipment used to separate water from environmental sludges. Based on the results of bench scale studies, the process can reduce the amount of water in the sludge by more than 50 percent, greatly reducing disposal costs. This promising technology is discussed in more detail in Chapter 3.

Electrodialysis. Electrodialysis is a desalting process driven by an electrical potential difference between oppositely charged electrodes. The principles of electrodialysis are used on certain emerging technologies, such as capacitive deionization. As applies to environmental applications, electrodialysis is a general category rather than a specific technology; therefore, it will not be considered further.

Electrohydraulic cavitation. This technology uses electrical energy to induce cavitation (i.e., the formation and collapse of small bubbles) in a water sample. The processes leading to cavitation produce shock waves and lead to the release of high-energy light. During cavitation various reactive species are formed, including hydroxyl radicals, hydrogen atoms and hydrogen peroxide. Electrohydraulic cavitation is induced using a spark-gap discharge in water or by ultrasonic irradiation. (It can also be induced using plasma discharges but that technology has additional uses so is dealt with separately). Preliminary research has identified a number of obstacles to full-scale use of the technology, but the results are promising enough to justify further discussion in Chapter 3.

Electrolysis. Electrolysis is the use of electrical energy to effect a chemical change. It is commonly used in a number of different industrial processes, but its principal environmental application is in electrocoagulation. Electrocoagulation, which is a well-established treatment process and fairly common in industry, avoids the use of additional chemicals to remove solids from a process stream. However, a new system promises improved performance. This improved system is discussed in more detail in Chapter 3. A related technology uses cerium ion (Ce^{4+}) to catalyze oxidation reactions in hazardous waste. In the process, the cerium ion is oxidized to Ce^{3+}, but converted back to its original oxidative state electrochemically. This promising technology is also discussed in Chapter 3. Finally, one researcher has demonstrated that in-situ remediation of hazardous waste sites can be accelerated using electrolysis. This advancement is also discussed in Chapter 3.

Electron beam irradiation. Beams of high-energy electrons can be used like lasers to cut, drill, weld and heat treat metals. In addition, when added to a water or waste matrix the electrons generate various oxidative and reactive species, leading to advanced oxidation processes. Electron beam processing is an emerging technology that is worthy of further study, so it was considered in Chapter 3.

Electromagnetic leak detectors. In a typical U.S. water utility, between 5 and 20 percent of treated water is lost through leaks in the distribution system. Thus, identification of leaks is a key component in a utility's management plan. While important, these types of detectors are available commercially and so were not considered in Chapter 3.

Electroosmotic dewatering. This technology uses an imposed electric field to force ionic constituents to migrate to their attractive electrodes. This phenomenon has been successfully used in the ceramics industry for product dewatering, as well as in the construction industry for soil dewatering at building foundations and for migration of friction-decreasing water films to pile surfaces during driving. Researchers have used this process on a bench scale to dewater a variety of agricultural products, including animal manure, without the drawbacks of thermal water removal. The technology could have extensive applications in environmental applications where water must be removed, so it is discussed in more detail in the next section.

Electrophoresis. When an electric field is applied to a solution, electrically charged particles migrate across a solution to the opposite charge. The process, which differs from electrodialysis in the use of an electric field rather than an electrode, has proven to be uneconomical at large scales but is used commercially in many small-scale applications encountered in biological and medical research. Further, the principals of electrophoresis are used often in other electrotechnologies. Thus, electrophoresis was not considered further.

Electrostatic precipitation. This technology is employed widely in the air pollution control field. Stack gases are passed through an electric field to improve the removal of charged particulates. While this technology could benefit from research leading to improved methods, it is commercially established and thus was not considered further.

Enhanced gravity separation. Gravity separation is one of the most common water treatment processes in use today. However, a Canadian company has developed an enhanced process using specialized fluids to accelerate the separation of heavy metals from wastewater. While the system shows promise, the energy use requirements are small, so this technology was not considered further.

Freeze concentration/crystallization. As water molecules freeze they form a crystalline structure, pushing any other particles interspersed within the mixture out of the crystal. Freeze concentration takes advantage of this phenomenon to separate solids from water in sludge, greatly reducing the amount of sludge that must be disposed. EPRI, among others, has proven the effectiveness of this process in pilot-scale evaluations, but significant research is needed to address certain problems and improve process economics. This system is considered in more detail in Chapter 3.

Heat pump evaporation. This technology uses heat pumps in a conventional evaporative process to concentrate polluted waste streams. Significant advancement has been made in heat pump technology by various manufacturers, so this technology was not pursued further.

High temperature plasma-arc heater/furnace. Plasmas are often considered the fourth state of matter (besides gas, liquid and solid), but can be best described as ionized gases, which contain many highly reactive species. High-temperature plasmas are formed by heating a gas to a very high temperature (10,000°C or higher). This plasma can be used in a furnace to vitrify waste materials, greatly reducing the hazardous nature of difficult-to-dispose wastes and improving the

waste's stability for ultimate disposal. This emerging technology is highly promising and is considered further in Chapter 3.

Ion Exchange. Ion exchange is a common physical-chemical treatment process where specialized resins are used to extract ions from a waste stream. Contaminated water is pumped through the resin so that the harmful ions are exchanged with more benign ones incorporated into the resin. For instance, heavy metals in polluted water can be exchanged for sodium ions. The biggest drawback to existing ion exchange techniques is its nonspecificity. So, while the technology is quite common, one researcher is developing a specialized resin that targets specific contaminants. So while ion exchange has limited energy-related issues, the specialized resin is regenerated using a proprietary electrochemical process. This enhancement is discussed in Chapter 3.

Incineration. Several electric-based technologies can be used to incinerate solid, liquid and gaseous wastes. Resistance technology, which is commercially available, is used in molten glass incinerators and in high-temperature fluid wall reactors, which are a new type of incinerators. Other incinerator designs employ infrared heating and plasmas. Emerging, alternative incinerator designs will be dealt with in Chapter 3.

Infrared drying. Infrared radiation can be used to dry environmental sludge. Electric infrared emitters have lower overall capital costs and a higher efficiency, and can reduce gaseous emissions commonly encountered with fossil fuel-driven dryers. Infrared drying technology is an emerging one with great promise, and is discussed in more detail in Chapter 3.

Low-temperature plasmas. Low-temperature plasmas are ionized gases generated at ambient temperatures (see **High-temperature plasma-arc furnace** description above). There is a significantly smaller concentration of reactive species produced in low-temperature plasmas than in high-temperature plasmas; nonetheless, this technology is suitable for treatment of gaseous wastes or relatively clean water. Given the promising nature of this emerging technology, it is considered further in Chapter 3.

Mechanical vapor recompression. In mechanical vapor recompression evaporated gases are compressed to improve the energy efficiency of a concentrator. MVR has many uses in various industrial settings and could be widely used as a brine concentrator for desalination plants. However, it is a mature technology and so was not considered further in this study.

Membrane separation. In the past ten years enormous strides have been made in the science and use of membrane separation. The three principal types of membrane separation, including microfiltration, ultrafiltration and reverse osmosis, differ in the nominal size of the particles which can be removed. A relatively new application uses membranes initially developed for geotextile applications (developed as landfill liners or for stabilizing steep slopes during construction) in aerated lagoons or to dewater sludge, but uses little energy. A more futuristic effort in membrane research is the result of the collaboration of membrane experts, material scientists, and chemists. These researchers are developing "smart" membranes, which could selectively remove targeted pollutants without removing bulk constituents, such as calcium ions. However, this research is very preliminary and, at this time, there are no prototypes available.

Given the immense amount of research and significant inroads into use made by membranes today, this technology was not considered in Chapter 3.

Photocatalytic oxidation. Oxidation can be accelerated in the presence of certain wavelengths of light to treat wastes in a process termed photocatalytic oxidation. In fact, the combination of UV and ozone to generate advanced oxidation processes (as discussed above) is one form of photocatalytic oxidation. While the kinetics behind this technology are poorly understood, there are numerous applications in a variety of industrial and environmental applications along with several vendors marketing this equipment. Given its widespread use, it was not considered further.

Phytoremediation. The U.S. Environmental Protection Agency is promoting the use of native plants to remove pollutants from hazardous waste sites, which is a process also known as phytoremediation. In fact, wetlands treatment could be considered one type of phytoremediation. While the research needs for this emerging technology are immense, there is virtually no energy used so this technology is not considered further.

Pyrolysis. Pyrolysis is combustion in the absence of oxygen. Organic matter thermally decomposes in pyrolysis and yields oils of varying composition. The process greatly reduces the volume of waste and can produce substances with sufficient heating value to be used in cogeneration. Various firms are active in the field with at least one vendor marketing equipment; however, given its emerging nature the technology would benefit from additional research. Thus, it is considered in Chapter 3.

Ozonation. When molecular oxygen (O_2) is passed through an electric current a portion of the oxygen is converted to ozone, or O_3. Ozone is a highly reactive chemical which, under the proper circumstances, leads to advanced oxidation processes. Worldwide, the ozone industry is mature, particularly in Europe, but also in the United States. Many ozone applications in environmental fields are established; however there are a few emerging applications considered in Chapter 3 for specific waste disposal problems.

Supercritical water oxidation. When the temperature and pressure of water is brought above its critical point (where pressure equals 22.1 Mpa and temperature equals 374°C), water exhibits unique characteristics, many of which are particularly advantageous for environmental treatment. Supercritical water oxidation is an emerging technology which takes advantage of these properties to effect waste treatment. Given the technology's great promise, it is considered in Chapter 3.

Ultraviolet radiation. Ultraviolet light exhibits excellent germicidal properties at certain wavelengths. In addition, UV radiation can transform molecular structures making it useful in several industrial applications, such as pulp bleaching and in the curing of specialized coatings. However, this technology is well-established with a number of reputable vendors of UV systems. Given the technology's maturity, it was not considered further.

Vacuum pyrolysis. A Canadian firm has developed a process where waste is thermally decomposed under reduced pressure. Byproducts are withdrawn from the reactor by a vacuum

pump and recovered through condensation in the form of pyrolytic oils. Initially developed for the pulp and paper industry, the system may have many environmental applications. Thus, it is considered further in Chapter 3.

Wet air oxidation. Wet air oxidation is a liquid phase reaction in water using dissolved oxygen to oxidize wastewater contaminants. The oxidation reactions, which occur at moderate temperatures and pressures, typically results in the conversion of organic contaminants to biodegradable short chain organic acids. Inorganic constituents such as sulfides and cyanides can also be oxidized, and the process can be used for high strength wastewater streams prior to final biological treatment. While there are few commercial applications of the technology, there is little effort or interest in the technology and it cannot be considered an emerging one, so is not considered further.

3
QUANTITATIVE ASSESSMENT OF ELECTROTECHNOLOGIES

This chapter summarizes the efforts made to take those technologies identified as using energy and not yet commercially viable (in Chapter 2), describe their status and possible applications, and assign a quantitative score to the technology. First, the quantitative scoring method is described. Next, each technology chosen for screening from Chapter 2 was assessed. These assessments include a short description of the technology, its research and development status, a summary of potential applications, one or more references, and a preliminary score based on the scoring method described below. Finally, potential applications of the technologies are summarized in Table 3-2 and a preliminary quantitative ranking of the technologies is presented in Table 3-3.

Quantitative Scoring Method

Based on discussions with the staff from the California Energy Commission, there are five principal criteria for assessing the technologies, including: 1) applicability of the technology to multiple industries; 2) potential for funding from others besides the CEC; 3) current status of technology development; 4) possible impact of the technology on California industries; and 5) the potential for economic competitiveness of the technology in the future. Each criterion is discussed more fully below. The screening system used to develop a score on each technology is summarized at the end of this section.

The Commission, in an effort to improve the value of their research money, wants the focus technologies developed from this assessment to have a broad number of environmental applications. Thus, the first screening criterion measures the cross-cutting nature of the technologies. The broadness of the technology ranges from 1 (limited) to 5 (general use). The potential for the use of these emerging technologies and applications in potable water, wastewater (either domestic or industrial), air pollution, solid waste and hazardous waste is noted in Table 3-2, which is presented at the end of this chapter. Generally, the score given each technology was equal to the number of applications noted in Table 3-2.

The second criterion measures the support the technology could receive from others, ranging from 1 (no other support) to 5 (multiple agencies or companies interested). The CEC is most interested in providing ‘seed’ money to assist in technology development, but recognizes it cannot be the sole source of development funds. The score given a particular technology was based principally on the technology’s coverage in the environmental literature.

The third criterion assesses the current status of the technology. As mentioned previously, the CEC is most interested in those technologies that are yet to be developed. Three scores were possible for any technology, including already in commercial status (score of 0), demonstration units available (score of 3) and bench scale only (score of 5). The status of the emerging technologies is also included in Table 3-1.

The fourth criterion is a measure of the potential impact to California's industries. Technologies with the greatest potential impact receive the highest scores. For instance, a technology that could prove beneficial only to fruit processors might score very high given the extreme importance of fruit processing to the California economy. This criterion provides the evaluator with a method for giving a higher score to some of the more focused applications with a potentially large impact to one or more California industries.

The final screening criterion was the potential for the technology to compete economically with existing alternatives. This screening step recognizes that the current developmental nature of the technologies means that most are currently not economically competitive with existing alternatives. Further, the development process that will follow this report is intended to improve the economics. Thus, this criterion was essentially a judgment as to whether the technology could possibly become competitive.

The screening criteria are summarized below. The highest score possible for any single technology is 25. By assigning scores in all five criteria, the system enables the development of a subjective assessment of each technology and a means of prioritizing the list.

Table 3-1
Scoring Methodology

Applicability of Technology				
1	2	3	4	5
Limited applicability		Some different applications		Many possible applications
Potential Interest by Others				
1	2	3	4	5
No other interest		Some limited interest		Wide interest in technology
Technology Status				
1	2	3	4	5
Commercially viable		Demo units available		Bench scale only
Potential Impact to California Industry				
1	2	3	4	5
Little		Large impact on small California industry		Large impact on large California industry
Potential Competitiveness				
1	2	3	4	5
Will be too expensive				Very likely as or more competitive

Table 3-2
Potential Applications of Selected Technologies

Technology	Potable Water	Waste-water	Solid Waste	Hazard Waste	Air Pollution	Comments	Targeted Contaminants
Activated Carbon - Electrosolv	x	x		x	x	Limited to regeneration of granular activated carbon; applications reflect potential uses for the carbon	Contaminants which can be absorbed by carbon; principally organics
AOPs -Electrochemical Process Utilizing Nb-doped TiO_2 Electrodes	x	x		x		Potential improvement to conventional advanced oxidation processes; (i.e., generates hydroxyl radicals)	Organics, metals in water
Air Flotation	x	x		x		Improvement to existing process	Metals, fats, oils and grease
Capacitive Deionization	x	x				Very promising alternative to conventional desalination techniques	TDS, metals
Dielectric Heating		X	X	X		Currently has broad application in food processing; could have application in removing water from contaminated wastes.	Soils & sludge contaminated with volatiles and semi-volatiles, scrap tires, asphalt reclamation, medical wastes
Electrodewatering	x	x		x		Potentially a significant improvement to conventional dewatering processes, which are a notorious problem area for some water/wastewater systems	Sludges
Electrohydraulic cavitation by sonolysis (ultrasound)	x	x				Science behind process not well characterized; anecdotal evidence suggests effectiveness	Hazardous wastes, microbes

Table 3-2
Potential Applications of Selected Technologies (Continued)

Technology	Potable Water	Waste-water	Solid Waste	Hazard Waste	Air Pollution	Comments	Targeted Contaminants
Electrolysis (electrocoagulation)	x	x		x		Potential improvement on well-established technology	Metals, colloidal material, emulsions
Electrolysis (cerium-catalyzed advanced oxidation process)		x		x		Potential improvement to conventional advanced oxidation processes; (i.e. generates hydroxyl radicals)	Organics, metals, mixed wastes, low-level radioactive wastes
Electrolysis Electrokinetic Remediation of Groundwater				x		In-situ groundwater remediation technique offers great promise, but limited to single enviro application	Some organics, radionuclides, metals, most inorganics
Electroosmotic Dewatering	x	x		x		Bench scale technology with possible broad environmental uses	Sludges, certain agricultural products
Electron Beam	x	x		x	x	Technically feasible but too expensive for immediate commercialization; can oxidize and reduce contaminants	Halogenated solvents; nonhalogenated aromatics, oxidizable inorganics, flue gas scrubbing, med wastes
Freeze thaw conditioning			x	x		Conditioning process for sludges with immense potential to increase solids content, thereby reducing disposal costs.	Industrial and municipal sludges
High Temperature Plasmas	x	x	x	x	x	Emerging technology with broad potential	Organics, pesticides, dioxins, inorganics, etc.
Incineration			x	x		Existing application with several new methods	Organics, inorganics, metals, solid wastes

Table 3-2
Potential Applications of Selected Technologies (Continued)

Technology	Potable Water	Waste-water	Solid Waste	Hazard Waste	Air Pollution	Comments	Targeted Contaminants
Ion Exchange - Selective Ion Recovery System	x	x				Represents an improvement to conventional ion exchange processes	Arsenic, nitrate, chromium
Low Temperature (non-thermal) Plasmas	x				x	Emerging technology with broad potential in air treatment	Organics, metals, NOx
Ozone Ozonation of Rice			x			Specific application of value to state of California	Would eliminate rice straw disposal problem
Ozone Control of NOx					x	Specific application of value to California with air pollution concerns.	NOx from flue gases of IC engines
Ozone Modify Shredded Tires			x			Specific application which could greatly increase the recycling of discarded auto tires, a major waste disposal issue	Waste tires present disposal problem, fire hazard
Pyrolysis & Vacuum Pyrolysis			x	x		Emerging technology with broad potential in solid & hazardous wastes	Organics, pesticides, dioxins, etc.
Supercritical Water Oxidation	x	x	x	x		Emerging technology with broad potential is nearing commercialization	Organics, inorganics, pesticides, dioxins, all recalcitrant pollutants
Ultraviolet Disinfection of Metal Removing Fluids				x		Novel application of an existing technology to deal with an emerging and significant waste disposal problem	Microbes in metal removing fluids

Table 3-3
Suggested Ranking of Technologies

Rank	Technology	Score					Total
		Applicability	Interest	Status	Impact	Compete	
1	Electrodewatering	3	5	5	4	4	21
2	Capacitive deionization	2	3	5	4	5	19
3	Dielectric heating	3	4	3	4	4	18
	Supercritical water oxidation	4	4	3	4	3	18
	AOPs using Nb-doped TiO_2 electrodes	3	3	5	4	3	18
	Freeze thaw conditioning	2	4	3	4	5	18
4	Electron beam irradiation	4	4	3	4	2	17
	Ion exchange – selective recovery	2	3	3	4	5	17
5	Low temp (non thermal) plasmas	2	4	3	4	3	16
6	Activated carbon - Electrosolv	4	2	3	2	4	15
	Electroosmotic dewatering	3	2	5	3	2	15
	High temperature plasmas	5	2	3	4	1	15
	UV disinfection of metal removing fluids	1	4	3	2	5	15
7	Electrolysis – Cerium catalyzed AOP	2	2	3	4	4	14
	Electrolysis-electrokinetic remediation	1	4	3	2	4	14
	Ozonation to modify shredded tires	1	2	3	5	3	14
8	Electrohydraulic cavitation by sonolysis	3	2	5	2	3	13
	Ozonation of rice straw	1	2	3	4	3	13
9	Air flotation	3	3	0	2	4	12
	Electrolysis – electrocoagulation	3	3	0	3	3	12
	Incineration	2	4	0	4	2	12
	Ozonation for control of NOx	1	4	0	3	4	12
	Pyrolysis & vacuum pyrolysis	2	2	0	4	4	12

Description and Status of Technologies

While the principal focus of this study was initially on emerging technologies, it was quickly noticed that there are a number of established technologies that may be applied in a broader manner, or in a unique application. These types of applications are emerging in the sense that the efficacy of the application is unknown and significant engineering hurdles must be overcome before commercialization. Short summaries of the technologies and applications are presented below.

Activated Carbon Absorption & Electrical Regeneration – the Electrosolv® Process

Description & Status

This process, developed and promoted by a company based in Massachusetts is a unique and patented process for regenerating granular activated carbon (GAC). GAC is widely used to remove VOCs in water and air from industrial processes. The VOCs are adsorbed until the pores of the carbon are full and no further adsorption can take place. GAC is conventionally regenerated by heating the carbon to a temperature of 150-200^{o}C and purging the bed with gas.

GAC can be regenerated using steam, an inert gas, or thermally. In each case, VOCs are released and flushed away during the regeneration process. The Electrosolv® process regenerates the GAC by heating the carbon using an electric potential across electrodes placed at each end of the GAC bed. The GAC is an electrical resistor, so the carbon can be heated directly and temperature can be controlled by varying the voltage. A relatively pure VOC stream is driven off from the carbon, and can be removed by vacuum, or a small flow of purge gas, and condensed for reuse or disposal. According to the manufacturer, this system has been successfully tested at a landfill gas project in New York to remove vinyl chloride from the landfill gas. However, scale-up issues and demonstrations on other applications are needed. This technology is limited to the regeneration of GAC, although GAC has numerous applications in addressing environmental problems. Its use is limited somewhat by the fact that using it generates another disposal problem. It is rarely economically viable to regenerate small volumes of GAC. This system may improve those economics, making GAC a more viable solution. Typical industries which could benefit from this process include semiconductor manufacturers and metal fabricators.

Applications: Water contaminated with low concentrations of organics, such as potable water sources and tertiary wastewater treatment, along with certain industrial wastewater streams.

Preliminary Score: **15**

Reference: http://www.foster-miller.com/elecsolv.htm for developer's website.

Advanced Oxidation Processes Electrochemical Advanced Oxidation Process Utilizing Nb-doped TiO_2 Electrodes

Description & Status

This technology is a novel advanced oxidation process in which water is electrochemically oxidized to produce hydroxyl free radicals. The system consists of an anode and cathode immersed in the waste stream. The anodes consist of a titanium metal substrate with an oxide coating comprising titanium dioxide (TiO_2) doped with 4 mole percent niobium (Nb) or tantalum (Ta) in the +4 valence state. Both elements are commercially available. Niobium is rather inexpensive while tantalum is more rare and, thus, more expensive. The oxide coating is a heavily doped semiconductor, and the resulting electrodes have excellent corrosion resistance at the high potential needed to generate hydroxyl ions. If the developer's claims are correct, this process may be a more efficient (and thus less costly) means of generating advanced oxidation processes than conventional methods.

The electrodes are produced by baking a coat of TiO_2 doped with Nb on to a titanium metal substrate under conditions that favor the +4 oxidation state of Nb. Methods have been developed to produce rod electrodes and disk electrodes for laboratory use. Subsequent improvements have allowed production of plate electrodes of titanium sheet and porous electrodes of titanium fiber. Porous anodes are produced by coating bundles of 50 μm diameter Ti fibers with the same metal-doping composition. The time needed for water to flow past a fiber is only 0.5 ms, and the thickness of the diffusive boundary layer formed is on the order of 1 μm, allowing excellent mass transfer.

This technology has been demonstrated on the bench scale, so there is now a need to construct a prototype water treatment unit with a treatment capacity in the range of 10 to 40 liters per minute. The prototype units would operate at about 30% current efficiency and 6V cell voltage, corresponding to 67 kWh/kg chemical oxygen demand (COD) destroyed. Research is needed to improve electrode life, current efficiency, and reaction kinetics at small concentrations of contaminant. At least a two-fold improvement in energy cost is expected as the electrodes and process conditions are optimized. Typical industries which could benefit from this process include municipal water and wastewater and auto plants.

Applications: Wherever advanced oxidation processes are used, including removal of organics from water, oxidation of heavy metals and taste and odor-causing compounds, treatment of landfill leachate, and for tertiary treatment in water reuse schemes.

Preliminary Score: **18**

Reference: Hoffmann (2001)

Air Flotation - Bubble Assisted Flotation

Description & Status

Air flotation is a common technology for removal of fine suspended solids that are difficult to filter or remove by settling, such as fats, oils and grease. In the mining and metals industry, commutated ore is concentrated by use of a polymer and air flotation in what is called froth flotation. Another version of the process saturates a slurry with air under pressure, and than flashes the fluid to produce tiny bubbles of air that float the suspended solids, with removal by skimming. This latter process is called dissolved air flotation (DAF).

The major difficulty with DAF is the limitation on how much air can be dissolved in a fluid under pressures attainable in economically feasible equipment. Typically, equipment costs limit DAF to a fluid-to-air ratio of one or less. Bubble assisted flotation increases the ratio, by means of a bubble chamber in which the fluid enters tangentially, forming a thin liquid layer which circles along the wall of a porous center tube through which air is forced under pressure. As a result, the fluid-to-air ratio can be varied from less than 1 to 1 to greater than 1 to 100. The bubble chamber process increases the bubble particle interaction by several orders of magnitude, and allows optimization of bubble size, so that flotation happens within a few milliseconds. The aerated fluid flows to a vessel for skimming and separation. Bubble-assisted flotation units are lower in capital and operating cost, and take up far less space than a conventional DAF unit.

According to the manufacturer, several commercial applications of this technology are now in operation. Air flotation systems are becoming fairly common in pulp and paper mills and water treatment facilities.

Applications: This process would compete against existing uses of dissolved air flotation, which is in widespread use in a wide range of industrial wastewater plants, including mining, petroleum/chemical, food and agriculture, and ceramics.

Preliminary Score: **12**

Reference: http://www.cleanwatertech.com/waterdance.html for company website

Capacitive Deionization

Description & Status

The heart of the capacitive deionization system is layers of a carbon fiber-based mesh that serves as electrodes. The layered mesh is arranged in such a fashion that when a direct electric current is applied the polarity of the layers alternates. The dissolved salts in the water are attracted to the layer with the opposite polarity, thus removing the dissolved salts from the water. When sufficient dissolved salts are deposited on the electrodes so that the conductivity of the electrode increases beyond the set point desired, the electrodes are regenerated by shorting them to ground.

The contaminants essentially 'fall off' the electrode and are flushed from the system. The waste, at 5 to 10 times the original concentration, is discharged through a valve to drain. Upon completing discharge of the waste, the polarities are reversed and the cycle is renewed.

A principal advantage of capacitive deionization over the conventional alternative, reverse osmosis, is that pretreatment is not a major issue. The factors that affect membranes and resin such as suspended solids, chlorine and organics do not affect the electrodes of the system. Indicative of the interest in this technology, researchers at the U.S. Bureau of Reclamation believes that this technology is one of the most promising developments in the field of desalination in the past twenty years. While preliminary results are very encouraging, the largest flow to be treated to date is 3 gpm. Thus, there is a need to assess scaling issues. This technology would have widespread applicability in potable water treatment.

Applications: This technology will be an alternative to desalination technologies, such as reverse osmosis, and for the treatment of brine wastewater discharges.

Preliminary Score: **19**

Reference: http://www.sabrex-tx.com/ for company website

Dielectric Heating

Description & Status

Dielectric heating encompasses the use of high frequency electromagnetic radiation to generate heat. Two wavelengths of radiation are used, including radio frequencies (longer wavelength) and the higher frequency (shorter wavelengths) microwaves. Radio frequencies (RF) have been used experimentally to mobilize hazardous wastes contaminating soils. The process works by inserting a large grid of electrodes spaced from 10 to 50 feet apart. Application of the RF leads to volatilization of contaminants entrained in the soil, so a vapor barrier is installed over the remediation site to collect the vapors for subsequent treatment. Thus, it is ideally suited for the treatment of soils contaminated with volatile organics and aliphatic compounds, along with semi-volatiles. A conventional microwave oven works in a similar fashion but uses microwaves from 300 to 3000 MHz to generate heat within the target substance. There has been little use of dielectric heating processes in environmental processing outside of some hazardous waste sites.

RF heating has been found to be effective at removing hazardous wastes from small areas, typically less than 1 acre and no deeper than 20 feet. Significant amounts of buried metals interfere with the process' effectiveness, and the properties of the soils must be carefully considered before implementing the process. This process has found limited application in full-scale remediation, but there is a tremendous need for a better understanding of the science to better optimize its use. Commercial RF heating equipment is used heavily by the food processing industry, but there has been little use of the process for environmental applications. Thus, RF heating of industrial and municipal sludges is worth investigating. One possible application is described in detail below.

Applications: Potential applications are numerous and range from the removal of volatile organic compounds from solids, such as contaminated soils, to assist in the separation of oil/water mixtures (as described below).

Preliminary Score: **18**

Reference: Bellandi (1995) www.pscrfheat.com

Possible Dielectric Heating Application: Microwave of Oily Steel Mill Sludges

Preliminary results from a bench study suggest that this treatment could have a huge impact on the steel industry. The U.S. steel industry generates over 400,000 tons of steel mill sludge each year. Oil and grease removal exceeded 95 percent in all tests. Current disposal costs range between $ 20 and $ 35 per ton, with costs expected to increase as environmental regulations become more stringent. Operating costs for this technology are estimated about $ 20 per ton of sludge, but the value of the recovered iron oxide and oil is approximately $ 15 per ton of sludge. Thus, the technology could generate savings of $ 15 to $ 30 per ton of sludge which translates into savings for this industry of $ 6 to $ 12 million per year. Further, there are many other industries with oily wastes that rely on rather inefficient oil-water separators, where this system will probably have applications.

Reference: EPRI (1996) www.cmu.edu/cmri/adm_areaMTIW.html

Electrodewatering

Description & Status

An Australian research group has equipped a conventional filter belt press with a DC powered electric system which applies an electric field to the sludge during dewatering. The field imposes an extra electroosmotic driving force on the dewatering which results in an increase in both the rate and extent of moisture reduction. The system has been demonstrated on the bench scale to improve the solids content of municipal wastewater sludge from approximately 20 % to greater than 40 % solids. Researchers are currently attempting to retrofit a full-scale unit and operate the system continuously to assess process economics.

The system has the best potential for widespread use in urban areas where disposal of municipal sludges is difficult or expensive. In addition, the system could find broad application with other industrial pollution problems where sludge is generated, such as with pulp and paper mills and steel mills. However, these applications will require additional laboratory research.

Applications: This technology is primarily suited for biosolids (i.e. wastewater sludge) and, to a lesser extent, water treatment residuals. The technology will enhance water removal, thereby reducing the volume of sludge for ultimate disposal.

Preliminary Score: **21**

Reference: Condie & Miller, 2000

Electrohydraulic Cavitation by Sonolysis

Description & Status

The introduction of high power ultrasound waves (i.e. sound energy with frequencies in the range 15 kHz to 1 MHz) into liquid reaction mixtures causes a variety of chemical transformations. Ultrasound frequencies are those beyond human hearing. Transducers are used to convert the electrical energy into sound waves, which in turn induces cavitation within the water. Research suggests that transducers employing higher frequencies provide far less power and penetration than those in the lower kHz range. Higher frequencies seem to have a significant effect on free radical formation.

Ultrasonic irradiation induces electrohydraulic cavitation, which is a process during which the radii of preexisting gas cavities in the liquid oscillate in a periodically changing pressure implosion of the gas bubbles. The rapid implosion of a gaseous cavity is accompanied by adiabatic heating of the vapor phase of the bubble, yielding localized and transient high temperatures and pressures. Temperatures on the order of 4200 K and pressures of 975 bar have been estimated.

Dissolved gases in the water serve as the nuclei for the formation of cavitation within the solution. The cavitation occurring around the nucleation sites leads to very high temperatures and pressures around the areas of these bubbles (on a very small magnitude). The high temperatures and pressures lead to the formation of free radicals and high electrical fields, which in turn leads to redox reactions and possible disinfection. While the technology has been of interest to researchers for most of the 1990s, it is still very much an emerging one for environmental applications. EPRI cosponsored a demonstration by the Water Environment Research Foundation that used sonolysis for disinfecting wet weather flows. Based on very poor performance obtained from the initial study, the work was suspended. However, it was recognized that additional research and development could produce a working prototype. The relatively low score of this technology is a reflection of the significant difficulties facing successful commercial development of this technology. A unique application of this process would be with keeping zebra mussels off of water intake structures.

Applications: This technology could have numerous possible applications, including recovering oils from soils, decomposing PCB's, degrading toxic wastes, reacting with water-based pollutants, and (perhaps) disinfection.

Preliminary Score: **15**

Reference: Mason & Luche (1997); Jensen (1998)

Electrolysis – An Improvement on Existing Electrocoagulation Practices

Description & Status

Electrocoagulation is a technology that has been used successfully for many years, mainly in the treatment of metal plating and mining wastewater for the removal of heavy metals, and the treatment of produced water from oil/gas production to remove colloidal material and oil emulsions. In these applications, sacrificial aluminum or iron electrodes are electrolytically dissolved to produce a metal oxide floc that absorbs the heavy metal ions and is removed by flocculation and settling.

Recent research suggests that there are mechanisms other than adsorption and flocculation involved in the process. It is now clear that the production of ions at the anode during oxidation produces double layer compression, followed by charge neutralization when electrons flow through the water. These effects increase removal efficiency from bridging and entrapment that occur when the floc formed creates a sludge blanket that entraps colloids that have not complexed, but are removed during settling.

A new process development, consisting of stainless steel cathodes and iron anodes in a tubular configuration, appears to be a significant breakthrough in removal efficiency and cost. Water flows through the ladder of cells by way of a labyrinth of holes in the cathode. This system has been successfully tested on leachate from mining spoils, landfill leachate, municipal sewage (primary clarifier influent), and lake water for potable uses. In all cases, the results were impressive, including reduction of bacterial load. This may represent an advancement for a well-established technology that may achieve dramatic improvement in treatment cost and efficiency for many difficult wastewater streams.

Applications: This technology could be used to remove a number of contaminants, including turbidity, inorganics, BOD, COD, and oil and grease. It will compete against existing coagulation methods, which are principally chemically-based.

Preliminary Score: **12**

Reference: Mills (2000)

Electrolysis - Cerium-catalyzed Electrochemical Oxidation Process

Description & Status

The CerOx® process, developed by a private California company is an electrochemical oxidation process catalyzed with elemental cerium. Cerium is a rare earth metal commercially available for a modest cost in a number of forms. The process has promise as a safe and economic alternative to incineration for many industrial waste streams. Incineration of hazardous wastes, which is

controversial and a difficult process to site, produces fine particulates from incomplete combustion, and dioxins from chlorinated waste streams.

In the CerOx® process, wastes are injected into solution and treated at low temperature (100°C) in enclosed tanks. Classified as a tank system, the process is exempt from the Resource Conservation and Recovery (RCRA) regulation (that governs disposal of hazardous wastes). According to the manufacturer, the process can handle a wide range of concentrations at flow rates up to 50,000 gallons per day; however, this claim must be independently verified.

According to the developers, projected operating costs should be comparable to incineration, but capital costs are expected to be less than half that of incineration. The process involves metering organic wastes into a liquid phase reactor through an ultrasonic mixer that emulsifies the immiscible material to maximize contact with the cerium reactant solution. Gaseous products are vented to a counter-current packed-bed gas phase reactor in which the exhaust gas comes in contact with the cerium solution. The solution oxidizes hydrocarbons and oxygenates to carbon dioxide and water. The final two reactors in the process are a unit containing an electrochemical cell stack that regenerates the cerium, and a neutralizer for chlorine and other acid gasses.

Applications: The developers claim the process treats a wide range of contaminants in water, primarily those amenable to oxidation; these include dioxins, PCB's, phenols, mixed wastes, cyanides, and low-level radioactive waste.

Preliminary Score: **14**

Reference: http://www.ehs.unr.edu/cerox/index.html (results of pilot assessment)
http://www.cerox.com/ for developer's website.

Electrolysis - Electrokinetic Remediation of Groundwater

Description & Status

A Texas company has developed a range of efficient in-situ soil and groundwater treatment technologies, that can be adapted to a variety of site and contamination characteristics at very low treatment cost ($30 - $100 per m^3) and with extremely low energy consumption (20-50 kWh per m^3 of soil yielding energy cost only 10-20 % of the total treatment cost). The technologies are based on in-situ application of low energy electrical fields, which induce electrokinetic (EK) phenomena in soil that are beneficially used in soil and water cleanup. The electrokinetics can efficiently operate in low permeability soils where most contamination accumulates. The current produces an acidic environment, which leads to desorption of the contaminants from soil particles. In this manner, the concept is very similar to the selective ion recovery process described earlier.

Current technologies, such as incineration or storage at landfills, require excavation and transportation of contaminated soil or water, which yield high costs ($400 – $1,000 per m^3 of soil). The developers have demonstrated removal of metals and radionuclides from soil, enhanced bioremediation for treatment of soil polluted by organic contaminants; formation of

impermeable, cementitious barriers for containment of contaminant plumes (e.g., in leaky landfills), and formation of permeable, reactive barriers for active reduction of dense-non-aqueous liquids (DNAPLs) using electrokinetic techniques. Further, the developers claim to have demonstrated electrokinetically enhanced phytoremediation for removal of heavy metals. However, mixed contamination has never been treated using combined in-situ technologies, so additional research is needed to perform a field demonstration of a combined in-situ process for treatment of soil and/or groundwater contaminated by mixed metal and organic contaminants. If successful, this process would be effective at removing metals, radioactive inos, some organics and most inorganics from contaminated soils at hazardous waste sites. This technology, which is still only in the small-scale demonstration phase, could have widespread applicability at hazardous waste and brownfield sites.

Applications: This technology is suited for treatment of contaminated groundwater at hazardous waste sites or in brownfield development for a wide variety of contaminants.

Preliminary Score: **14**

Reference: EPA (1995)

Electroosmotic Dewatering

Description & Status

Under an imposed electric field, ionic constituents in product water tend to migrate to their attractive electrodes and, in an immobile solid matrix, the migrating ions exert a frictional drag which induces an accompanying flow of water molecules. The electroosmosis phenomenon has been successfully used in the ceramics industry for product dewatering, as well as in the construction industry for soil dewatering at building foundations and for migration of friction-decreasing water films to pile surfaces during driving. Its benefits in these operations are well established.

EPRI and the University of Georgia have found that electroosmotic dewatering is feasible in removing water from certain types of agricultural crops and wastes, including sweet potato extrusions, peanuts and wastewater sludge. These bench scale assessments suggest that there could be widespread environmental applications, too. However, the technology is quite preliminary and untested.

Applications: Its principal use would be in reducing bound water in environmental sludge and biosolids, thereby reducing the volumes to be disposed through landfills, incineration, or other means. Typical industries include pulp and paper mills, chemical plants, and steel mills.

Preliminary Score: **15**

Reference: EPRI (2001)

Electron Beam Irradiation

Description & Status

Generated electrons react with water molecules to form hydroxyl radicals, reducing aqueous electrons, and hydrogen radicals. These reactive species oxidize or reduce the organic and inorganic compounds present in the water. The amount of energy transferred to an irradiated material is not constant as the electrons penetrate deeper into the material. Energy transfer near the surface is less than maximum transfer, which occurs at approximately one third to one half of the maximum depth of penetration. The maximum depth of penetration is directly proportional to the energy of the incident electrons and inversely proportional to the density of the material being irradiated. Electron beam irradiation has current commercial uses in welding, plastics polymerization, medical equipment sterilization, and food processing. Irradiation of aqueous solutions with high-energy electrons results in the rapid formation of excited state species and free radicals.

The greatest technical challenge associated with electron beam use for environmental uses is that, even at very high energies, the very small mass of the electron means that they do not penetrate into the water very deeply. For instance, electrons generated with a 1.5 million volt accelerator operating at 50 milliamps will penetrate only about 7 millimeters into water. Thus, the water flow must be spread over a thin layer, oftentimes using a weir, before applying the electron beam. This requirement presents significant scale-up challenges. Electron beam accelerators in the energy range of 1 to 5.0 MeV with power capacities up to 100 kW are commercially available, but their application in water and wastewater treatment is still emerging. Considerable progress has been made in reducing the accelerator size while maintaining or increasing the beam energy to improve process economics. Principal applications would be to remove pollutants (both oxidizable and reducible) from various water sources, including hazardous wastes, potable water supplies, and wastewater.

Applications: A quite broad technology, electron beam irradiation could treat oxidizable and reducible pollutants from potable water supplies and wastewater streams, hazardous wastes, and medical wastes. Industries that would benefit from this technology include the healthcare field and metal fabrication shops.

Preliminary Score: **17**

Reference: Cooper, et. al. (1992) – an excellent background paper
Anonymous (1995); EPRI (1998a); EPRI (1998b)

Freeze-thaw Concentration/Crystallization

Description & Status

Freeze-thaw conditioning of sludge (i.e. solids intermixed with water) improves the separation of the solids entrained in the sludge from water. The technique is practiced through natural means by numerous water treatment plants in the northern portions of the U.S. However, this project seeks to achieve the same benefits for generators of sludge in more temperate portions of the country, which includes much of the state of California.

In freeze-thaw conditioning, the sludge is frozen using commercially-available freezer equipment. The frozen sludge is crushed and allowed to thaw naturally. Freezing alters the chemical bonds between the solids in the sludge and the water, making the sludge more easily dewatered. It is particularly effective on sludge containing hydrated metal salts, such as alum. The conditioned sludge is then processed using conventional sludge dewatering equipment. Conditioning the sludge increases the amount of water that can be removed from the sludge. Thus, the total volume of sludge disposed (in landfills or by hazardous waste contractors) can be greatly reduced. In fact, preliminary EPRI results suggest that the process may already be economical for hazardous wastes.

EPRI has conducted a number of demonstration studies with the concept. However, there is a tremendous need for systematic assessment of the freezing process to better understand it. Further, there is significant potential to implement energy-efficient practices during the process. Many questions could be answered by a detailed demonstration project.

Applications: This technology, is principally a conditioning process; it improves the dewatering of municipal and industrial sludge but will not reduce or otherwise effect pollutant concentrations. Typical industries to benefit from this technology include the food processing industry.

Preliminary Score: **18**

Reference: EPRI (1998b)

High Temperature Plasma Processing

Description & Status

Plasmas are ionized states of matter containing electrons and ions. When generating plasmas from matter, the electrostatic forces that normally bind electrons to atomic nuclei are overcome, so that the plasmas consist of two commingled populations of oppositely charged particles-electrons and ionized nuclei. Plasmas are found naturally on Earth only in lightning and the aurora, but much of the sun is made of plasma as are the stars. Further, plasma science is the fundamental component to the study of fusion energy, and finds many applications in such different areas as the sterilization of medical equipment, surface etching of semiconductors, and the missile-defense systems under development by the Department of Defense.

There are two principal methods of generating plasmas. The first method generates plasmas from matter using very high temperatures (high temperature plasmas), while the second method uses

electrical energy to energize electrons exiting the other gas species at near-ambient temperatures (low temperature plasmas). Low temperature plasmas are discussed in a subsequent section.

High-temperature plasma processing consists of heating a gas to very high temperatures. The two principal types of high-temperature plasma processing techniques include transferred and nontransferred arcs. In the nontransferred arc, the plasma torch is passed between two electrodes. In the transferred arc, the plasma is formed directly between a single electrode and the material to be processed. Transferred arcs are well-suited for the treatment of solids while nontransferred arcs work best in processing toxic liquids and gases.

Temperatures in the center of the arc plasma are in the range of 10,000 to 20,000°C, and the temperature of solid material processed by arc plasma range from 1,600 to 2,000°C. The high temperatures provided by the plasma melt virtually anything so that, upon cooling, the material is vitrified slag, which is a highly stable form suitable for disposal in landfills. It is necessary to supply an external fuel source to obtain the high temperatures used in high temperature plasma processing. Preliminary research suggests that total costs could be in range of $ 100 to $ 200 per ton of waste and that energy requirements could be less than 1,000 kWh per ton. Test systems utilize a variety of designs, both water-cooled copper and graphite-electrode technologies. The systems are most appropriate for solid waste, hazardous wastes, and biological wastes.

Applications: Applications of high temperature plasmas would be quite broad because they promote the formation of advanced oxidation processes; their chief application would be in the removal of recalcitrant organics in the treatment of solid waste, hazardous wastes and biological wastes.

Preliminary Score: **16**

Reference: Anonymous (1995); Elmore and Lee (1999); www.startech.net

Incineration

Description & Status

Incineration technologies rely on high temperatures to effect chemical changes to pollution problems. It is principally suited for bulk solid or highly concentrated liquid hazardous wastes, such as spent solvents or PCB-laden transformer oil. Several incinerators are currently commercially available, and include electric arc furnaces, induction furnaces, and resistant furnaces. However, there are some emerging incinerator designs that have the potential for improving incinerator economics. These newer technologies include the high-temperature fluid wall reactor and the pyrolytic incinerator, and would be the focus of any additional developmental work.

A description of incineration would be incomplete without addressing the political difficulties associated with installing incinerators. Many environmental groups and citizens' rights groups collaborate to oppose the siting of any new incinerators, which they oppose on the basis of air emissions. Based on scientific evidence, incinerators are excellent at reducing the volume and

toxicity associated with a variety of wastes. However, new incinerators oftentimes face numerous permitting and regulatory hurdles before they can be built and operated. This factor, while difficult to quantify, is an important consideration for an agency interested in getting as much leverage as possible for any research dollars committed to developing a technology.

Applications: Incineration can be used to destroy hazardous wastes, solid wastes, and municipal biosolids.

Preliminary Score: **14**

References: Bellandi (1995)

Ion Exchange - Selective Ion Recovery System

Description & Status

The selective ion recovery system, promoted by a California firm, uses a new ligand-based process to selectively recover toxic anions from aqueous solutions. The process uses inexpensive, highly selective media, which extracts contamination but not benign ions. It is a closed loop process that extracts the targeted contaminant in a stable, non-soluble form. The media used is a ceramic powder with secure bulk supply and rapid adsorption kinetics. A simple caustic flush regenerates the media, and preliminary research demonstrates that there is no capacity loss even after more than 50 regenerations.

A proprietary electrochemical process can be used to recover the contaminant in a benign form. The caustic based regenerant can be reused in a closed loop process. Researchers have demonstrated that the process can reduce chromate (VI) concentrations from 120 ppb to less than 2 ppb, perchlorate concentrations from 18 ppb to less than 2 ppb, and arsenic concentrations from 100 ppb to less than 1 ppb in a three gallon per minute waste stream at an aircraft manufacturing plant. Independent assessments by EPRI experts suggest that this process is, at a minimum, a superior method of ion exchange for the specific removal of nitrates, arsenic or chromium. The potential potable water applications in economically removing nitrates and arsenic are huge. Bench-scale evaluations are completed but there is a need for demonstration studies.

Applications: This technology will compete against specific pollutant removal technologies. Currently, developers use the system to remove arsenic and nitrates, which are conventionally removed using either activated alumina, ion exchange, or membrane technologies. Semiconductor manufacturers rely on ion exchange and so would benefit from this process.

Preliminary Score: **17**

References: EPRI (1995)

Low-Temperature Non-thermal Plasmas

Description & Status

In low-temperature plasma formation, electrical energy is used to excite electrons, or make them "hot" (increased temperatures by few to tens of eV temperature) while the remaining gaseous species are "cold" (near ambient temperatures). Low-temperature plasmas operate at atmospheric pressures so that the decomposition of the toxic materials is principally accomplished by the interactions of the waste constituents with the excited electrons and free radicals generated by the reactions of the electrons and other gaseous species. The various plasma species, which include electrons, ions and neutral species, are not in thermal equilibrium, so they have different temperatures (and, thus, different average kinetic energies).

There are six principal forms of reactors used to generate non-thermal plasma, including silent discharge (or dielectric-barrier discharge), packed bed, pulsed corona, surface discharge, glow discharge and radiofrequency (RF) discharge. Because the glow- and RF-discharge reactors usually operate with high efficiency at lower pressures and, consequently, lower throughput, they are not strong candidates for pollutant processing. The other four types are suitable for environmental applications.

Applications: The technology is suited for the removal of dilute concentrations of pollutants in airstreams, including VOCs, organics, inorganics and other compounds. Tanneries and meat packers would benefit from this technology.

Preliminary Score: **16**

References: Rosoch (1997)

Ozonation – Innovative Applications

Ozone is an established technology with several vendors who manufacture and sell ozone equipment worldwide. However, given its broad applicability, new uses are continuously under development. For instance, the Food and Drug Administration recently awarded ozone "Generally Regarded as Safe" (GRAS) status for its use in the processing of food products. The following three applications are emerging ones and particularly pertinent to the state of California. Researchers from California companies and institutions are currently assessing the three possibilities to meet a significant environmental issue that is challenging state environmental officials. The specific applications are discussed in detail below.

Application No. 1 - Ozonation of an Agricultural Waste Stream into a High Energy Animal Feedstock

Description & Status

Several million tons of rice straw are produced in California each year. Environmental regulations discourage field burning. Existing uses for this material do not begin to utilize the production. This technology could convert rice straw into an animal feed equivalent to alfalfa hay, which is in short supply.

Rice straw is considered to be a significant environmental waste stream in California and throughout U.S. rice production regions. After harvest of the grain, the rice stalks must be removed from the field rather than incorporated back into the soil. The traditional agronomic practice is to burn the rice straw either in the field or after collection. However, incineration of the rice straw can lead to air pollution problems, particularly near nonattainment areas as defined by the Clean Air Act.

The high levels of an indigestible component of rice straw--called lignin--also prevents the use of rice straw as a significant feedstock for ruminant animals. The amount of lignin in a plant stalk is the most significant factor that limits the availability of structural carbohydrates in consumed plant material to anaerobic respiration by ruminant species. Recent studies by California researchers have demonstrated that ozone may be quite effective at destroying or disrupting the lignin structure in rice straw. This approach allows for chemical release of the soluble cellulose fraction in ruminants without leaving any residue in the final product.

The researchers have found that the useful cellulose portion of rice straw is not affected by ozone treatment while the unneeded lignin and hemicellulose portions are degraded. Ozone can potentially be used to degrade lignin in a wide range of poor quality forages and crop residues (i.e., rice straw, buffalo grass, rice hulls) and subsequently increase digestibility.

Researchers have just begun to understand the operating conditions and associated engineering controls needed to safely load the straw, introduce the ozone gas and control the heat that is generated in the container, and thermally destroy any residual ozone remaining in the container or in the effluent gas stream. Despite these advances, further development of the rice straw treatment container and ancillary control equipment is needed before commercial development can proceed.

Applications: The technology is strictly limited to addressing the rice stalk disposal problems of the California rice industry.

Preliminary Score: **13**

References: O. Murphy (2001)-personal communication
http://agronomy.ucdavis.edu/uccerice/main.htm

Application No. 2 - Ozone for Control of NO_X in Stack Gases

Description & Status

An interesting new technology currently being marketed is the use of ozone to control NO_X emissions from flue gas. The control process is based on the reaction of ozone with nitrogen oxides in combustion gas, (mostly NO and NO_2) to N_2O_5, which is highly soluble in water, and is removed in an aqueous scrubber. The process consists of an induced draft fan to move the gas through the system, two heat exchangers to reduce the flue gas temperature to below 350°F, an ozone generator, and an ozone NO_X reactor, followed by a wet scrubber. The two heat exchangers can be replaced by a direct contact evaporative quench, if high quality heat exchange is not desired.

Unlike selective and non-selective catalytic reduction, or pre-combustion NO_x mitigation techniques, the low temperature oxidation process recovers useful heat, which along with the sale of emission credits for industrial applications are expected to provide a payback on the capital investment of 3 to 5 years. The process has been tested on a 400 hp gas fired boiler, and has achieved NO_X reduction from 144 ppm to below 2 ppm. Operating the system to achieve removal to below 4 ppm NO_X in the exhaust can generate emission reduction credits (which are currently as high as $2500/pound), which can further improve economics. The technology is applicable to industrial boilers and co-generation in non-attainment regions, where recovery of waste heat can be utilized in the process, or to preheat boiler feed water. It is expected that this process could work on any standby generators, including those fired by natural gas and those fired by diesel fuel.

Given the current situation in California, where energy conservation and emission reduction from power generation are of great importance, this process is worth consideration. A large number of stand-by or emergency generators at industrial facilities, hospitals, wastewater plants etc with many megawatts of capacity are constrained from operation by terms of their emission permits. This technology could enable many of them to be permitted for continuous operation. A demonstration could quantify the benefits and economics of the system.

Applications: This application is limited to the control of NOx from flue gases, and could be applied to any fossil fuel-based electric generator.

Preliminary Score: **12**

References: http://www.boc.com/gases/solution/environmental/air_pol/nox.htm

Application No. 3 - Ozone-based Surface Modification of Crumb Rubber for Improved Asphalt Blends

Description & Status

It is estimated that there are approximately 300 million tires discarded each year in the United States, in addition to the estimated 800 million scrap tires that already reside in landfills. The

ultimate objective of the tire recycling community is to develop technologies that will consume more tires than what are presently discarded. One of the most interesting and promising large volume uses for rubber from scrap tires is as a road building material, chiefly as an additive or supplement to asphalt. Industry experts estimate that, if universally adopted at a moderate level of 60 pounds crumb rubber per ton of asphalt (about 3 percent by weight), rubberized asphalt could consume 2 billion scrap tires annually.

Ground tire rubber, when well digested and highly cured into asphalt, improves binder performance-grade properties. In the short-term, both low-temperature thermal cracking resistance and high-temperature pavement rutting performance properties are improved to provide an increased temperature performance span. A second, long-term, effect arises from improvements in the aging characteristics of asphalt. High-cure crumb rubber binders exhibit reduced oxidative-aging hardening rates, rates that are lower by as much as fifty percent. This reduces hardening rates and should significantly improve pavement life.

California is one of the few states that utilize rubberized asphalt in pavement construction on a regular basis. Even though there are many economic and environmental benefits to using rubberized asphalt in highway construction, there are also disadvantages that have prevented this process from being used on a wider scale**.** The high temperature required to cure the rubberized asphalt properly is an energy intensive process that adds significant cost to the overall construction project. Also, heating the rubberized asphalt mix to elevated temperatures can result in the release of potentially hazardous organic compounds, such as dioxins, into the atmosphere surrounding the processing plant. As most of the processing is done on-site, expensive portable scrubbing and monitoring systems are required.

A California company has developed an ozone-based surface modification treatment for crumb rubber that enables the rubber particles to undergo enhanced chemical interaction with asphalt. According to the process developer, the asphalt produced using the ozone treated crumb rubber has been shown to exhibit improved settling characteristics, have better high temperature viscosity, and show improved resistance to fatigue and thermal cracking over conventional crumb rubber/asphalt formulations. Most importantly, these results were achieved at lower cure temperatures and shorter cure times. Research is needed to demonstrate a full-scale treatment system capable of generating large quantities of the modified crumb rubber for blending into asphalt.

Applications: This use of ozone is limited to processing rubber from scrap tires to reduce a significant solid waste disposal issue in California and throughout the country.

Preliminary Score: **14**

References: O. Murphy (2001)

Pyrolysis and Vacuum Pyrolysis

Description & Status

Pyrolysis is the chemical decomposition of organic materials by heat in the absence of oxygen. A completely oxygen-free atmosphere is impossible to obtain, so in a practical sense pyrolytic treatment of wastes are defined as those where heat is used with less than the stoichiometric quantities of oxygen. By minimizing the amount of oxygen used to treat wastes, oxidation reactions, and the associated byproducts, are also minimized. Pyrolysis has the greatest potential effectiveness on treatment of soils and sludges contaminated with a variety of organic contaminant groups, such as halogenated and nonhalogenated volatiles and semivolatiles, PCBs, pesticides, dioxins and organic cyanides and corrosives. A specific, but significant, application is in the destruction of scrap tires. Pyrolysis will not be effective with inorganics, oxidizers and reducers. It is important to note that there are a number of ways to pyrolize substances, including molten glass incinerators, advanced electric reactors, infrared incinerators and plasma incinerators.

A subset of pyrolysis is under development by a Canadian company, which pyrolizes hazardous wastes under a slight vacuum. The system, which is marketed under the trade name Pyrocycling™, allows pyrolysis to occur at lower temperatures and pressures than used with atmospheric pyrolysis and incineration. This reduces the need for high-strength materials of construction and the maintenance costs associated with the unit.

There are a few vendors currently market equipment specifically for pyrolysis, so pyrolysis must be considered commercially available. Most of the data to date has focused on bench scale systems, so there is a need for demonstration-scale data. Demonstrations are needed to identify engineering needs and potential process economics.

Applications: Pyrolysis is well suited for nearly any solid or hazardous waste. Given its high energy needs, it is most appropriate for hazardous wastes or contaminated soils where other disposal options, such as landfills, are expensive or dangerous.

Preliminary Score: **16**

References: Kreitmeyer & Gardner (1996); http://www.environaccess.ca/fiches_4/F4-03-95a.html

Supercritical Water Oxidation

Description & Status

Supercritical water oxidation has existed as an emerging technology for several years. The technology is based on the unique properties of water at conditions above its critical points (i.e. temperatures above 374 C and pressures greater than 220 bar (3208 psi). Under these conditions,

both inorganic matter and gases, including oxygen, are completely miscible in water, whereas inorganic salts exhibit greatly reduced solubility, and thus precipitate from solution. As the waste streams are heated and pressurized to water's critical points, mass transfer constraints disappear and oxidation reactions proceed rapidly to completion.

Supercritical water oxidation is self-sustaining for wastes with a chemical oxygen demand in excess of 15,000 mg/L. More dilute wastes need supplemental fuel, such as waste oil, while concentrated wastes may need to be diluted if the heat generated by the oxidation of the fuel cannot be readily removed from the containment vessel. The potential applications of this technology are quite broad, and include both inorganic and organic liquid and solid wastes, along with industrial and municipal sludge and solid wastes. Further, this is an excellent treatment for wastes containing nitrogen, which forms nitrates during biological treatment and NO_x during incineration. Gas effluents from this process are principally oxygen, carbon dioxide and nitrogen gas with little NO_x. General Atomics currently owns patent rights to a commercial system using this process. While some systems seem close to fruition, no commercial systems are in place. Perhaps the biggest question facing broad implementation of this technology is identifying suitable materials for reactor design. Consideration must be given to both general corrosion as well as pitting.

Applications: Supercritical water oxidation is suitable for treating organic wastewaters and sludges contaminated with halogenated and non-halogenated organic compounds.

Preliminary Score: **18**

References: Kreitmeyer (1996); EPRI (1995b)
www.generalatomics.com/atg/aps/scwo.html

Ultraviolet Disinfection of Metal Removal Fluids

Description & Status

Metal removal fluids (MRF) are sprayed onto metal surfaces and tools to cool, lubricate and flush metal chips and abrasives during metal fabrication. Sales of MRF exceed $300 million in the U.S alone. Because of their cost (5 to 16 cents per liter), the treatment and recycling of MRF is extremely important to the economics of the metal fabrication industry.

Worker exposure to MRF is the most pressing environmental issue in the metal fabrication industry. There are an estimated 1.2 million workers in the U.S. continually exposed to machining fluids, and these exposures are suspected to have caused various cancers, respiratory diseases, and skin problems. Microbial contamination of the fluids is hypothesized to be a potential cause of these occupational diseases. Worker safety concerns will result in U.S. regulations drastically reducing the permissible worker exposure limits to MRF in the near future

There is a consensus that an effective fluid disinfection process is key to reducing worker health problems and extending the useful life of the fluid. Traditionally, chemical biocides have been

used for disinfection of MRF. Biocides are toxic themselves, and bacteria quickly develop resistance, necessitating increased dosage, and more frequent fluid replacement. Used MRF are disposed of as a toxic waste due to its content of toxic biocides and metals. In fact, it is estimated that several million pounds per year of waste MRF is sent from California metal fabrication plants to hazardous disposal sites each year. An effective, economic, non-chemical disinfection process should find rapid acceptance in the MRF business.

Pasteurization has been used to disinfect MRF for many years. It is, however, a batch process, requiring the removal of the fluid from use and heating to a specified temperature, followed by cooling and the return of the fluid to use. Unfortunately, the bacteria are quickly re-established unless chemical biocides are added. Ultraviolet disinfection has been attempted in the past, but the opacity of the fluid impedes penetration, and traditional broadband UV causes fluid oxidation. According to the developer, an advanced UV process has successfully solved these problems. The process uses a patented monochromatic UV source and a pump around reaction chamber to assure all portions of the fluid receive a germicidal dose. The UV output is in a single wavelength, minimizing photo degradation of the fluid.

Applications: Metal removing fluids are currently disposed in hazardous waste landfills. This technology would eliminate this sizeable amount of hazardous waste. Further, this assessment could be expanded to include other possible electrotechnology solutions, such as using membranes to recycle metal removing fluids.

Preliminary Score: **15**

References: www.t3i-uv.com for company website
www.aware-services.com/orc/environm1.htm

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Tables

Potential applications of the selected technologies are presented in Table 3-2. The summary of the rankings of the technologies given in Chapter 3 is given in Table 3-3.

4
PROMISING TECHNOLOGY SUMMARIES

Electrodewatering

Background

Disposal of biosolids is a significant issue for wastewater treatment facilities in the state of California. According to a 1998 survey, biosolids in the state of California are most often land applied, and costs associated with the hauling and disposal of the biosolids average between $ 80 and $ 170 per dry ton of biosolids. This cost is principally a function of the cost of hauling the material an average of 73 miles from the treatment site to the land applications site (OCWD, 1999). Typically, biosolids from a conventional belt filter press, which accounts for about one-third of all biosolids in the state, contains 75 to 80% percent water, which must be hauled along with the solids of during land application. More effective ways of removing the water from the biosolids would greatly decrease the volume and subsequently reduce the costs associated with land application.

Wastewater treatment plants in urbanized areas of Australia face the same problems. The local councils in Brisbane and along the Gold Coast spend over $AU 5 million in sludge management. In response to this need, an Australian research group, the Commonwealth Scientific and Industrial Research Organization (CSIRO), developed an electrodewatering unit that can greatly reduce the amount of water in biosolids. The researchers have developed a prototype which that applies the principles of electrodewatering on conventional belt filter presses. The prototype has worked very well on test sludges from Brisbane and the Gold Coast, but there is a substantial need for further demonstrations on biosolids generated from other wastewater treatment facilities using alternative processes.

Theory and Operation

In electrodewatering a direct voltage electric current (DC) voltage is applied to the suspension of biosolids. The application of the current voltage across the mixture leads to the creation of both electrophoretic and electroosmotic phenomena. In the initial stages of dewatering particles migrate to the electrode of opposite charge (i.e. electrophoresis). Once a cake is formed, electroosmosis predominates as ions migrate to the appropriate electrode to compensate for particle charges. Too much voltage leads to ohmic heating, which may not effect water removal but is an inefficient use of power.

The Australian group working on this project proposes to equip existing belt filter presses with electrodes to achieve electrodewatering benefits using conventional technology. A schematic of their proposed modified belt filter press is given in Figure 4-1. In the figure, DC voltage would be applied at the darkened rollers. The electrical effects would be pronounced as the dewatered solids passed over a portion of the belt filter press.

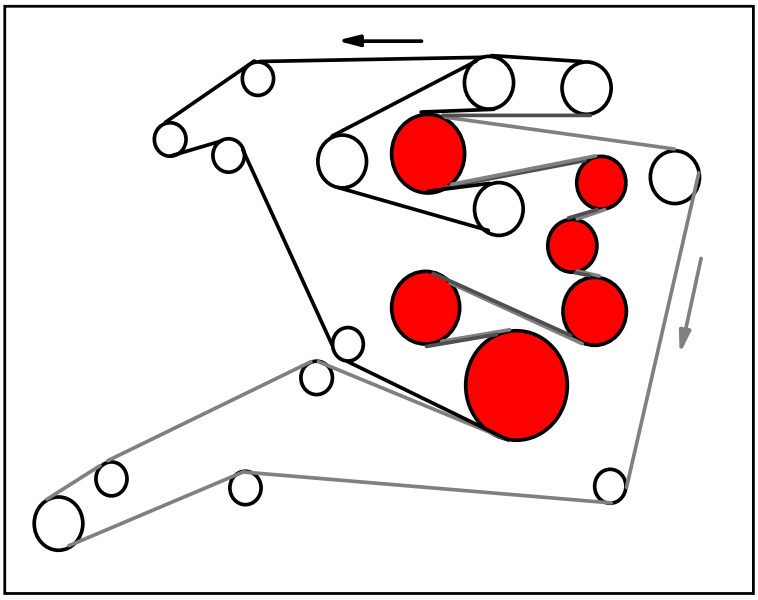

Figure 4-1
Schematic of Electrodewatering Unit

Electrodewatering has been attempted by numerous groups since the 1920s. The EPRI Municipal Water and Wastewater Program sponsored a demonstration of an electo-acoustical dewatering unit in 1995. In that study, an electro- acoustic dewatering process using electric and ultrasonic fields improved water removal over a conventional belt filter press by approximately 8 percent. Previous research, as noted above, demonstrates that the concept is technically sound. However, the bulk of the research efforts have focused on laboratory-scale assessments. Until recently, very little work has been done on developing a suitable system capable of meeting full-scale requirements or in optimizing such a system. The EPRI study in Dallas was a collaborative effort with a belt press manufacturer, Ashbrook-Simon-Hartley. The manufacturer provided the bench-scale assessments of electro-acoustic dewatering.

Past Research

Electrodewatering has been attempted by a variety of groups since the 1920s. Some of the recent research efforts are discussed herein. The Electric Power Research Institute (EPRI) Municipal Water and Wastewater Program sponsored a demonstration of an electo-acoustical dewatering unit in 1995. In that study, an electro-acoustic dewatering process using electric and ultrasonic fields improved water removal over a conventional belt filter press by approximately 8%. Previous research, as noted above, demonstrates that the concept is technically sound. However,

the bulk of the research efforts have focused on laboratory-scale assessments. Until recently, very little work has been done to develop a suitable system capable of meeting full-scale requirements, or to optimize such a system. The EPRI study in Dallas was a collaborative effort with a belt press manufacturer, Ashbrook-Simon-Hartley (1995). The manufacturer provided the bench-scale assessments of electro-acoustic dewatering.

Limited research has been conducted by others using electricity to enhance the dewatering of biosolids. Shang and Lo (1997) identified the processes behind electrokinetic dewatering of a phosphate clay. This process is well-established to dewater contaminated soil at hazardous wastes sites. They found that intermittent current and polarity reversal improved the effectiveness of the treatment. Banerjee and Law (1998) developed a laboratory system to characterize electroosmotic dewatering of two types of biomass, one of which was a wastewater sludge. Electroosmosis accounted for removal of an additional 13% percent of the sludge's water content. Gingerich [note: spelling in reference list is different]et. al. et al. (1999) conducted more detailed laboratory research on combining electroosmosis principles with pressure filtration. These researchers achieved final cake solids exceeding 50 weight percent when applying 60 V DC to the sludge. The researchers also found that further application of the electric current would lead to additional water removed. [Does "further application" imply higher current/voltage?] More recently, Ho and Chen (2001) compared electro-osmotic dewatering of betonite slurry using stationary and rotating anodes. The rotating anode speed varied between 0 and 300 rpm, and the researchers found that solids content improved by more than 70 % over that achieved by a stationary anode when anode speed exceeded 240 rpm. Further, the authors found that the energy consumption of the process was modest, requiring less than 20% percent of the latent heat of water evaporation.

Anticipated Costs

Sludge disposal costs are highly variable and depend on a number of factors, but the method used for ultimate disposal, and the distance between where the sludge is generated and where it is disposed of are extremely critical. Costs for sludge disposal in the state of California are highly variable. Land application is the most common ultimate disposal method in California. So land application of sludge that is generated in urbanized areas, far removed from land application sites, tends to be expensive. An electrodewatering system would be most attractive to an urban wastewater treatment plant that must haul their treated biosolids long distances to their ultimate disposal site.

The Australian research group launched their effort to solve the problems encountered in Sydney, which has a climate quite similar to that found in many urbanized portions of California. Miller et al. (1999) present cost estimates based on pilot scale studies of electrodewatering of sewage sludge in Sydney. Their study found that electrodewatering could reduce disposal costs by about $AUS 50 (approximately $ 25 in U.S. currency) per dry ton. Disposal costs in Brisbane are nearly $AUS 300 (approximately $150 in U.S. currency) per dry ton, which is on par with urbanized areas of California (OCWD, 1998), so savings are projected to be about 15% percent.

These anticipated costs per dry ton ($/DT) for electrodewatering are compared to costs for other technologies generated by EPRI in a recent study on water and wastewater treatment plant

residuals and biosolids. Those costs are compared in Table 4-1. A quick review of the table shows that the capital costs for electrodewatering are higher than the lower bound of capital costs for the other technologies. Moreover, maintenance and electricity costs for electrodewatering are among the highest. However, what is not shown in the table is the tipping fee reduction associated with disposal of a drier (and therefore less voluminous) product. Therefore, tipping fee reductions may significantly offset the higher operating and maintenance costs of electrodewatering. In addition, the capital costs are likely to be compatible with belt filter presses since electrodewatering is in essence a modification of the belt filter press, and capital costs are within the upper bound of costs for drying beds and centrifuges.

Table 4-1
Cost Comparison of Various Dewatering Technologies

Technology	Electricity Cost ($/DT)	Fuel Cost ($/DT)	Labor Cost ($/DT)	Maintenance Cost ($/DT)	Capital Cost
Lagoons	0	0	10.00	0	100,000
Drying Beds	0	3.00-4.50	7.00 - 14.00	1,250-17,500	125,000 to 1,750,000
Belt Filter Press	0.15-3.35	0	9.00-29.00	3,000-20,000	318,000 to 2,100,000
Centrifuges	1.50-34.00	0	15.00-40.00	1,500-7,500	145,000 to 160,000
Electrodewatering	70.00-140.00	0	9.00-29.00	5,000 – 24,000	500,000 +

A review of the costs indicates that current costs for electrodewatering are higher than the costs for standard belt filter presses. However, the technology is still under development. With continued improvements, costs should be comparable to belt filter presses because the process is a slight modification on belt filter presses. Increases in operating cost over conventional belt filter presses due to higher electricity use should be offset by the reduction in tipping fees associated with disposing of a drier (and therefore less voluminous) product.

Research Needs

The Australian group assessed the performance of electrodewatering in four different wastewater treatment plants. The four plants produced biosolids with solids content from 15 to 20 weight percent, which is typical for those using belt filter presses. Bench scale tests of the new system developed by the Australians produced solids contents of 38 weight percent to more than 53 weight percent. Electricity consumption ranged between 1,570 and 3,185 kWh per ton of dry solids, depending on initial conditions.

The researchers used the bench scale tests to build a prototype. Results from assessments of the prototype showed that energy use and performance could be greatly optimized over the bench scale results. In fact, their research demonstrated that energy use from the full-scale process was

less than 1,350 kWh per ton of dry solids. On average, the process removed nearly three tons of water per ton of dry solids and produced a cake of around 35 weight percent.

These results are encouraging but there is a significant need for further to optimization of the process. For instance, the electric use can be applied indefinitely (or at least until all water is removed) but the ohmic heating that results is generally an inefficient use of electricity. Additional research is needed to identify when to cease applying the electric voltage. The onset of ohmic heating varies depending on the composition of the biosolids, among other factors.

Recommendations for the California Energy Commission

Laboratory and bench-scale research for electrodewatering has made considerable progress is complete. However, in order to achieve market penetration, this technology must be tested on full-scale belt filter press dewatering equipment. The California Energy Commission (CEC) should consider funding demonstration projects of the technology on both wastewater treatment plants for both biosolids and industrial sludge. Modest demonstration projects, which could deliver satisfactory data on operating and maintenance costs and considerations, could be conducted for less than $ 200,000 based on past experience with these types of demonstration projects and discussions with the researchers in Australia.

Dielectric Heating

Background

Heat is used in a variety of environmental treatment processes. One of its principal uses for environmental applications is for the removal of bound water from hazardous sludges or semi-solids. Water removal greatly reduces the quantity of solid that must be disposed, which saves both transportation costs and tipping fees. Another common application for heat is in soil or water contaminated volatile organics. Heating the matrix leads to vaporization of the volatile organics, which are then collected for treatment and disposal.

Environmental applications have historically relied on convection or radiation techniques, such as gas-fired incinerators. Dielectric heating, on the other hand, offers several potential advantages to these conventional methods. Dielectric heating includes both microwave heating and radiofrequency (RF) heating, which differ in the frequency of the electromagnetic radiation used to achieve the heating. RF heating has been used commercially since the 1930s in a variety of industrial applications, and microwaves are a ubiquitous item in American kitchens, so the industry is mature. However, widespread use of the technology for environmental applications would require answering many engineering questions. In order to obtain these answers, feasibility assessments and significant investment is necessary.

Theory

Dielectric heating is based on a phenomena exhibited by non-metallic materials when absorbing high-frequency electromagnetic radiation. Polar molecules, which by definition have electrically charged poles, vibrate in the presence of an alternating electrical field. The friction from the vibration creates heat; all molecules within a substance vibrate, so that even ones located in the

center of substance are heated. In this way, dielectric heating is volumetric and is much faster than conventional methods that must rely on convection of the heat from the outside of the substance into its interior. Theoretically, another advantage of dielectric heating is that the surroundings are not heated during the process.

The electromagnetic radiation used for dielectric heating is in the frequency range of 300 to 300,000 MHz. However, the Federal Communications Commission (FCC) has set aside specific frequency bands dedicated for microwave heating to avoid any conflicts with communication equipment. Thus, in practice the most common frequencies used by microwave heating equipment are 915 and 2450 MHz while the most common frequencies for RF heating are 13.56 and 27.12.

Microwave power output for heating processes is produced by a special tube called a magnetron. A magnetron is a high vacuum electronic valve consisting of a hollow copper anode incorporating a series of resonance cavities, at the center of which is an electron emitting cathode. A magnetron generates microwaves in much the same way that one generates a tone, by blowing across the mouth of a bottle. The oscillation frequency has a wavelength proportional to the size of the bottle, so if the bottle is partially filled with water, the frequency of the acoustical tone generated increases. In a magnetron tube, the electron cloud generated by the cathode is the 'air' and the resonant cavities of the anode surrounding the cathode are the 'bottles'. As electrons leave the central anode they are induced into circular rotation by a magnetic field, passing many resonator 'bottles' before finally being captured by the anode. The result is microwave energy generated within a very narrow frequency bandwidth. Typical modern magnetron tubes operate at electrical efficiencies greater than 70% and will run without problems for more than 5000 hours.

There are several mechanisms by which matter absorbs microwave energy; however, the most common are dipolar rotation and ionic conduction. *Dipolar rotation* accounts for nearly 80% of the heating contribution at 2450MHz. Water is a polar molecule. As a liquid the water molecules in virtually any substance are randomly oriented. When the electrical field (from microwave energy) is imposed, the polar water molecules tend to become ordered, or aligned, due to their asymmetric distribution of unlike charge partners. As the electrical field dies down, the molecules return to their random (disoriented) orientation. The net result is a conversion of energy from electric field energy to stored potential energy in the material and then to stored random kinetic or thermal energy in the material. Typical microwave energy fields are able to pull into alignment only about 1 molecule in every 10^3 - 10^5 molecules.

Ionic conduction accounts for the bulk of the remaining heating contribution at 2450MHz. Ions, naturally present in natural water samples, will accelerate towards its an opposite charge when an electrical charge is imposed. This acceleration causes an increase in collisions with other molecules. The net result is electric field energy converted into ordered kinetic energy and then disordered kinetic energy or heat. The effect of dipolar rotation is strongly temperature and frequency dependent, while ionic conduction does not depend on temperature or frequency.

The differences between microwave heating and RF heating are not limited to their different frequencies. The lower frequencies and higher wavelengths used in RF heating make it more

suitable for thicker substances. So, it has found applications in textile processing, food processing, lumber drying, paper manufacturing and metals fabrication. Microwave heating provides greater intensity, with smaller penetration depths, because the frequencies used are much higher, and the corresponding wavelengths are much greater, so its principal advantage over RF heating is that microwave heating works at a much faster rate.

Past Research

Dielectric heating technologies have been employed on in a number of industries, but only recently have attempts been made to pursue potential applications in waste processing. A wide variety of systems are currently under development for waste treatment, and a few specific systems are commercially available for certain applications, such as the processing of infectious wastes and wastewater biosolids. However, many of these applications specific systems have few (if any) full-scale applications.

Van Loock (1997) summarizes microwave and high frequency energy for hazardous waste processing. Most uranium and plutonium components along with fission products have properties that make them amenable to microwave processing. The author did not list any commercial applications but did suggest that potential existed for infectious wastes, soil decontamination, solvent recovery and incineration.

Bathen et al. (1997) describes a method of using microwaves to regenerate absorbents used in the removal of volatile organic compounds from a waste stream. The researchers observed that removal increased with an increase in microwave power up to a certain point where the microwave energy accelerated the destruction of the zeolite. The researchers also found that conventional thermal methods needed three to five times more purge gas and temperatures more than 100°C higher than what was needed for microwave treatment.

BRC Environmental Ltd. of England has constructed a microwave pyrolysis system to break down scrap tires into carbon, steel cord, hydrocarbon oils and hydrogen-methane gas mixture. The system produces a product that is dry and friable, as opposed to conventional incineration that produces hot and sticky end products. An additional advantage is that microwave pyrolysis does not generate combustion byproducts such as dioxins, soot and ash. A schematic of the system is presented on Figure 4-2.

Sanitec, Inc. of West Caldwell, NJ currently markets a microwave system for infectious waste. The system is self-contained and can be installed in a trailer to make it mobile. In the system, infectious waste is shredded, moistened, and passed through a series of microwave treatment units. The microwaves heat the waste stream, leading to disinfection of the material. The disinfection process is assessed constantly using challenge testing of spores of *bacillus subtilis*. Once the material is sterilized, it passes from the system and can be compacted and disposed of in any landfill.

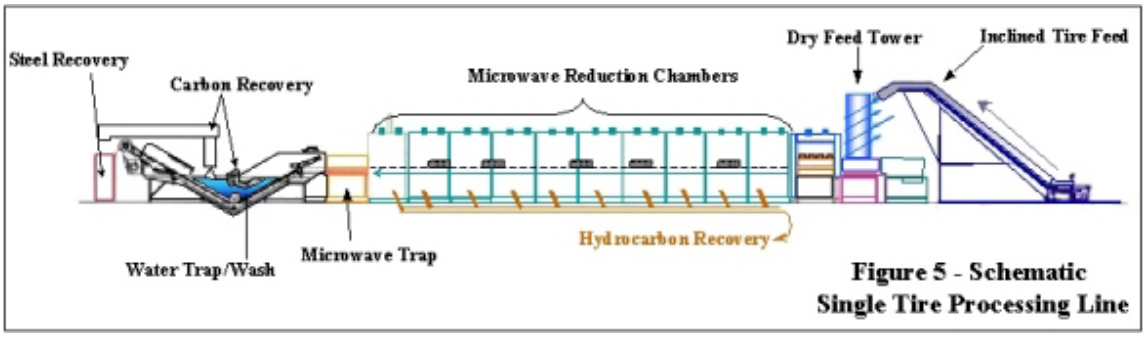

Figure 4-2
Microwave Processing Schematic

The microwave system uses approximately 270 kWh per /ton of waste processed. The company offers systems capable of treating up to 900 lbs per hour. The installed cost of a system capable of treating about 500 lbs. per hour was estimated to be about one-fifth of the installed cost of a conventional incinerator. The company claims nearly 20 different installations across the United States.

Energy International Inc. maintains the commercial license for the microGas SAGE system (microGas Corp., 1999). The SAGE system was demonstrated at a pilot study in King County, Washington in 1996. Wastewater biosolids are dewatered in a centrifuge to approximately 50% solids. The solids are then passed through a pyrolysis unit, which reduces the biosolids to char and ash. The char and ash are then passed through a microwave gasification unit that removes the char, high molecular weight organic compounds (i.e. tars), and the water vapor. During pyrolysis, the microwave unit produces a gaseous mixture containing hydrogen, carbon monoxide, methane and carbon dioxide, which can be flared our used to fuel cogeneration equipment. The ash exiting the microwave unit is nonhazardous so it can be disposed of in any landfill. According to company literature, this ash represents only 5% of the total volume of biosolids entering the system. According to the company, the capital cost of a 2,000 lb/hr system was estimated to range from $ 2.5 to $ 4.0 million, making them competitive when replacing a digester or gasifying digested solids.

EPRI (1992) demonstrated the feasibility of using microwaves to facilitate the separation of oil-water emulsions. Microwave processing greatly facilitated the separation of the emulsions and sludges into a form suitable for recycling and safe disposal. A pilot demonstration was proposed to identify full-scale operating considerations and economics, but this proposal died due to electric utility indifference and a slump in the steel industry economy.

The process required 8 to 12 kW per gpm of wastewater. The wastewater was generated from a steel mill hot strip rolling mill cooling water stream, and contained oil, polymers and metallic solids. Conventional de-emulsifiers could not separate the sludge, so the EPRI researchers adopted a two-step process. First, the oily metallic solids were concentrated using magnetic means, then the oily solids were microwaved after mixing with a release agent. A temperature rise of only 68 F (about 30 minutes of processing time) is needed to achieve excellent separation. Both of the separated streams are suitable for recycling. EPRI estimates that the operating and

disposal costs for this system would be $ 6 to $ 10 per ton versus current industry costs of $ 70 to $ 120 per ton for disposal costs alone.

Potential Uses

Radio-frequency energy is a potential heat source for a variety of food processing applications, such as blanching, drying, pre-cooking, concentrating, pasteurizing and sterilizing. Microwaves are currently used in the air dehydration of foods, and could find applications in freeze dehydration. A French manufacturer has developed a system that uses microwaves to concentrate heavy food slurries or whole food items. The unit has a drying capacity of four to seven liters of water per hour, which is much higher than conventional processes.

The U.S. Energy Research and Development Administration has funded a project to develop a microwave-vacuum system for drying grain. Results indicate that the system dries corn using 38 percent less energy than conventional dryers, using with temperatures that were 78°F higher and 73 percent faster. EPRI (1997) has also considered the use of dielectric heating to control insects and fungi in stored crops, and suggests that microwaves and radio frequency heating could be used to control pests in stored grains. Frequency, field intensity and heating rate are the three most important factors to be considered; insect mortality is principally a function of the final temperature within the grain.

Of more interest for this report, dielectric heating could find use in environmental applications in other, more specialized applications. For instance, Environmental Waste International of Ontario, Canada markets a microwave pyrolysis unit capable of treating up to 6,000 tires per day. The energy released by pyrolysis of that quantity of tires could generate up to 5.5 MW of electricity, half of which could be used in the processing and the other half would be available for sale. The scrape tires are loaded and air in the processor is replaced with nitrogen. Fifteen magnetrons deliver 900 kW of microwave energy leading to the breakdown of the scrap tires. Vapors containing hydrocarbons are directed to a scrubber to remove any hydrogen sulfide before recovering the gas for fuel. Steel and carbon black produced by the processing are separated in a water bath; the carbon can be reused in new rubber manufacturing while the steel can be recycled in conventional manners. The same pyrolysis process has been used to reclaim mixed wastes, such as plastics and metals.

Currently, radio frequency processing is used to volatilize organic compounds in contaminated soils. The electromagnetic radiation causes the organics to volatilize and migrate out of the soil matrix. These types of systems often have a vapor collection system installed over the contaminated area so that the volatilized compounds are not vented to the atmosphere. The condensed organics are collected and disposed of in an environmentally acceptable manner.

Estimated Costs

Dielectric heating cost estimates are available from a number of existing applications of the technology. However, many of these applications are rather limited in scope. So, while these applications give a rough approximation of the cost of the technology they also point the way to where research money would need to be directed to advance the use of this technology into greater commercial acceptance.

The EPRI study investigating the use of microwaves to separate oily wastes from steel mills lead to a detailed economic analysis (EPRI, 1992). In that study, the analysis was compared to the conventional disposal method of sending the material to disposal in a landfill. While the conventional disposal method was estimated to cost $ 490,000 to dispose of 7,000 tons of sludge per year, the microwave process could treat the same volume for just under $ 70,000 per year, assuming the use of 6,000 kWh of electricity per year and a unit electricity cost of $ 0.05 per kWh.

Cheremisinoff (1996) estimates that dielectric heating costs will vary depending on the system complexity and size. He estimates that a radio frequency dryer will cost between $ 1,000 and $ 3,500 per kW. Smaller ones, typically under 200 kW, will cost between $ 2,500 to $ 3,500, while larger units (up to 1,000 kW) will cost between $ 1,000 and $ 2,500 per kW. However, these estimates vary greatly depending on how the unit is designed. For instance, the cost for a continuous system with a 40 kW magnetron would cost between $ 100,000 and $ 160,000. On the other hand, a similarly sized batch unit would only cost $ 50,000.

The author points out that the chief advantage of a microwave system is the time savings available. A one-inch thick slab of frozen meat can be thawed in two hours using a microwave system compared to 15 hours by a conventional thawing method. However, the principal problem with dielectric heating is the significantly higher energy requirements to generate microwaves or radio frequency waves compared to steam. By one estimate, 10 to 20 Btu of steam heat is equivalent in energy value to one Btu of microwave power. Clearly, one emphasis of any further research must be the development of more energy-efficient magnetrons.

EPRI (1999) has developed a full-size and countertop microwave clothes dryer. The dryers consumed less energy than conventional electric dryers, and can be used to dry clothes that otherwise must be dry cleaned. A significant portion of the research effort has been on developing safety systems to address problems associated with “tramp” metal objects, such as bobby pins and nails that may heat enough to damage clothing. The safety system also addresses electric arcing and contains a gas detection system.

Recommendations for the California Energy Commission

Dielectric heating is an emerging electrotechnology for environmental applications with unique characteristics. A significant advantage for the California Energy Commission in pursuing this technology is that commercial units are available and could be adapted to new applications, so the questions to be answered are more related to engineering issues rather than theoretical concerns. For instance, units developed to treat medical waste or scrap tires could be used after

some modifications to remove water from industrial sludge. In addition, the radiofrequency system used at hazardous waste sites could be used to speed the removal of water from abandoned or full lagoons. Dielectric heating could be used in virtually any environmental application where water must be separated from a solid, including water and wastewater treatment, hazardous waste treatment, preparation of municipal solid waste for incineration (waste-to-energy), and in managing animal manure.

Based on the assessment of this technology, it is recommended that the California Energy Commission focus research money towards demonstrations of appropriate uses of dielectric heating in environmental applications and in any effort to improve the economics of dielectric heating. In addition, since the economics of dielectric heating are currently poor due to the high costs associated with generating microwaves, the CEC should pursue any effort to improve the economics of dielectric heating. In particular, bench-scale research into improving the efficiency of magnetrons should be considered for funding. Finally, demonstration will speed the acceptance of this technology by showing potential users the economic benefits. Dielectric heating is particularly suited for environmental applications which have historically been consider a necessary evil. Environmental managers usually give little thought to final disposal or to options to shrink the volume, so selling these concepts can be a challenge. Successful demonstrations from organizations like the CEC help the environmental managers overcome their skepticism and consider alternatives.

Capacitive Deionization

Background

According to the United Nations and the World Bank, approximately one billion people (about one-sixth of the world's population) lack adequate sanitation or drinking water. With continued population growth, this problem will only worsen unless technological solutions are found and developed to generate potable water. Only about 2% percent of the Earth's water is fresh water, and the bulk of this is locked up as ice at the planet's poles. Therefore, there is only a limited supply of fresh water reserves. Populations must rely on precipitation, which can fluctuate over time, or they must develop economically feasible techniques, such as desalinizing some of the vast quantity of sea water, in order to insure sustainability. California is not excluded from this scenario; it could face water shortages if recent growth patterns continue.

The water from the Colorado River is divided among users in Nevada, California, Arizona, Utah, New Mexico, Wyoming and Colorado. In the past, many states have not taken their share, and so California has often removed this "extra" amount. However, with recent growth and the completion of specific water resource projects, such as the Central Arizona Project, neighboring states will be taking their share from the Colorado River. The result will be that California will have to meet the needs of a larger population with less water. Clearly, alternative sources are needed.

Unfortunately, there are virtually no new fresh water sources available to state planners. Instead, increased demand will have to be met through water reuse, conservation measures, and

desalination of brackish sources or seawater. In fact, in many locales where agriculture plays a significant role in the economy, such as California, desalination may be the only solution. In the past, desalination plants have been expensive to build and operate. However, an advancement to an old process, known as capacitive deionization, offers significant promise.

According to the International Desalting Association, desalination plants built before the 1970s use thermal processes, and many of these use the waste heat from power plants to drive the processes. Recent advancements in membrane technology, particularly since 1990, have made these membrane processes more popular. As a result, most new desalination plants (particularly for those treating brackish water supplies) rely on membranes. Thus, any advanced technology, such as capacitive deionization, must be directly compared to membrane technology, with particular emphasis on the cost and performance differences.

Theory and Operation

Electrodeionization is the removal of ionized species from liquids using active media and an electrical potential to influence ionic transport. Ionics, Inc. developed and marketed an electrodialysis reversal (EDR) system to the water treatment industry that employed the principals of electrodeionization. Other manufacturers have also developed systems based on these same principles (DiMascio et al., 1998). Capacitive deionization is also based on these electrodeionization principles, but in this case the ion capacity properties of the active media are the primary sizing parameters. Both Lawrence Livermore National Laboratory (LLNL) and a small company in Texas have developed capacitive deionization systems. Farmer (2000) describes the LLNL system that uses carbon aerogel as the active media. EPRI funded some developmental work using the LLNL process to remove dissolved solids from Colorado River water, but the results were less than satisfactory. More recently, EPRI has worked with a product developer in Texas on a revised system. This system shows immense promise.

The Texas' company's system uses a series of electrodes, made from activated carbon fabric and a conductive material. When these electrodes are layered and a DC electric charge is applied, the individual electrodes are charged with different polarities. The dissolved salts in the water are attracted and loosely bound to the electrodes with the opposite charge, allowing the purified water to flow from the treatment unit.

As the dissolved salts deposit on the electrodes, conductivity increases. Once the conductivity increases beyond a desired set point, the electrodes are shorted to ground. The contaminants are rejected from the electrodes as ions and flow from the unit into the waste stream. After the regeneration, the waste (at 5 to 10 times the original concentration) is discharged through a valve to drain. Upon completion of this cycle, the polarities are reversed for normal operation.

Ionic species are removed according to first order kinetics, so the same percentage of dissolved solids is removed regardless of whether the feed stream is 500 to 15,000 ppm. Current systems are limited to raw water with a maximum total dissolved solids (TDS) concentration of 7,500 ppm. In the future, non-fiber based technology is being developed that will safely operate at TDS levels in the range of 15,000 to 35,000 ppm. (Seawater TDS concentrations average 33,000 ppm.)

Pretreatment of the water is not needed in capacitive deionization systems because the factors that can cause fouling on membrane surfaces, such as suspended solids, chlorine and organics, do not affect the electrodes of this capacitive deionization systems. The developer has also invested considerable effort into lowering operating costs, particularly as those related to electrical costs. The first innovation the developer used was to operate two identical units in series with so that the process could be operated at a higher voltage but a lower amperage power than a single unit. This allowed the use of lightweight electronics, which lowers the cost of the power supply and electrical circuitry. The second innovation used by the developer was a process termed "bleed and feed." In essence, the developer installed a recirculation line that takes a small portion of the treated water and recirculates it to the raw water feed. This has the effects of reducing the TDS concentration of the feed entering the purifier cell, and improving the TDS concentration in the system effluent. The end result is similar to that achieved by the process used for most commercial reverse osmosis systems, which use both series flow and recirculation valves to reduce ions in a stepwise fashion.

Current research revolves around the development of nanotubes so that the system could be used to desalinate sea water. Nanotubes are specialized materials characterized by high surface areas, high porosity, low density, and controlled pore size distribution (see additional information at www.nanopore.com). At the very high TDS concentrations common in sea water, capacitance increases rapidly with an increase in voltage for a carbon cloth capacitor. This means that, even at lower voltages a carbon cloth capacitor will become quickly clogged with ions when the process is used on sea water. Carbon nanotubes promise a better relationship between capacitance and voltage, which can be exploited in a capacitive deionization treatment system to better remove ionic species.

Past Research

Extensive research on capacitive deionization has been performed by Lawrence Livermore National Laboratories (LLNL) using carbon aerogel as the active media. Theoretically, carbon aerogel is a perfect media for such an application because of its excellent dielectric properties. DiMascio et al. (1998) summarize past efforts towards development of capacitive deionization processes. Much of the initial work occurred in the 1950s and 1960s, when several patents were issued for related devices. The first commercially available systems, however, were not introduced until 1987 under the trade name of Ionpure (now sold by U.S. Filter Corporation). Ionpure systems account for over 90 percent of the world's current installations of electrodeionization processes. However, they differ from the capacitive deionization systems described in this section in that the Ionpure system relies on a solid plate and frame arrangement where the compartments alternate as diluting and concentrating. While effective, the chief disadvantage of these arrangements is the potential for shorting to occur between various points on the plates. In fact, such short circuits are the primary reason for downtime in many water applications.

The concept used by LLNL is described under U.S. Patent No. 5,954,937 (Farmer, 1999). The system uses a serpentine flow pattern defined by electrodes. The electrodes are composed of carbon aerogel, and are insulated so that ion removal is achieved when an electric potential is applied across the electrodes.

Farmer (1996) describes LLNL's work with carbon aerogel as the active medium in a capacitive deionization process. With its extremely high porosity, carbon aerogel has an extremely high surface area to volume ratio, which makes the desalting process more efficient. The researchers claimed that their system could desalt brackish water (up to 3200 ppm total dissolved solids) at 10- to 20-times less energy than reverse osmosis. The system worked well enough that LLNL licensed the technology to Far West Group, LLC of Phoenix, Arizona. Far West in turn started a company, which they named Capacitive Deionization Technology Systems, Inc., to manufacture and install capacitive deionization units. In January, 2000, Far West entered into an agreement with ABB, Inc., the global technology behemoth, to develop and market the system.

Green (2001) assessed the system on Colorado River water and found that applied voltage controlled the degree of ion sorption. The sorption kinetics followed a Langmuir isotherm, and the aerogel had a greater affinity for monovalent cations than divalent cations. In addition, the researchers computed that only about 10% percent of the aerogel surface area was involved in the sorption process. Further, naturally occurring organic matter caused significant fouling.

Others have assessed both the feasibility of using aerogels for desalting water. Researchers with the University of Wuerburg's Center for Materials for Energy Research in Germany used carbon aerogels for high temperature thermal insulators and for broad band absorbers, but not for water treatment. Yeo et al. (1999) assessed the possibility of using aerogels in desalting and found some performance shortfalls.

Atlas (2000) describes the efforts of Sabrex, Inc. in developing the capacitive deionization process. They compared carbon aerogel, low speed carbon fiber cloth, and high speed carbon cloth as possible electrodes for a capacitive deionization material. They concluded that the carbon aerogel and low speed carbon fiber cloth would not work because of the high pore volumes and low density of these materials. The result in using these materials is that the system must first purify the interstitial pore volumes, rendering the material uneconomical. These findings lead them to consider the high pore volume carbon cloth. The researchers have used this information to develop a bench-scale system capable of treating water with a total dissolved solids content of 7,500 ppm or less.

Anticipated Costs

Power requirements for the bench scale system by Sabrex approached 8 kWhr per 1000 gallons to remove approximately 5000 ppm of total dissolved solids. This is approximately 20% percent higher than current electricity requirements for reverse osmosis. However, the developers are proposing two innovative additions to their system which will drive the energy use down. The first addition involves using a recirculation loop to improve the process operation. The other improvement will employ standard energy recovery techniques.

Based on their assessment of the improvements, the developers claim that ultimate power costs could be substantially smaller than current costs for reverse osmosis. This is demonstrated on Figure 4-3.

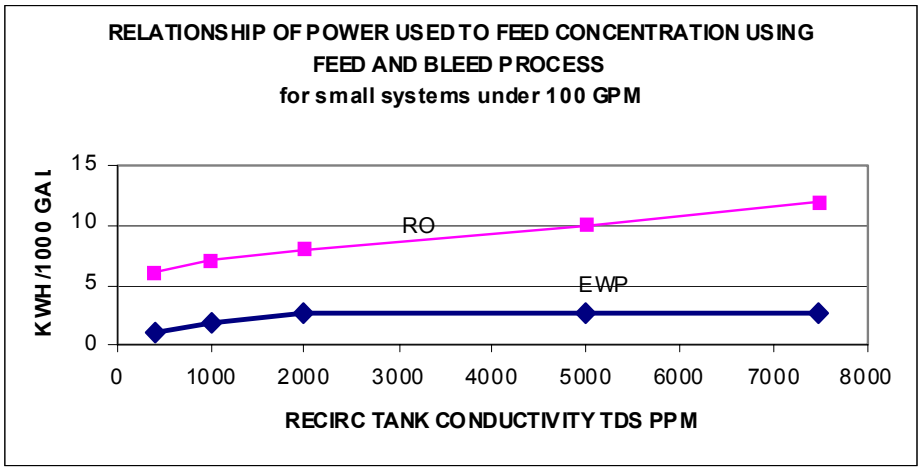

Figure 4-3
Relationship of Power used to Concentration in Capacitive Deionization System

The line marked EWP represents the capacitive deionization power use over a range of treated water conductivity. The system as proposed by the developers is more cost effective because as the total dissolved solids content of the feed water climbs, there is no corresponding increase in energy use. Reverse osmosis, on the other hand, requires an increase in power use with increasing levels of total dissolved solids.

Based on this assessment, the developers claim that with adequate research, the capacitive deionization process could have an operating cost that is approximately one-fifth the operating cost of reverse osmosis costs. Significant research is necessary to attain such an achievement, and would require a minimum of three years and more likely five years. Further complicating these projections is the great strides made by reverse osmosis membrane manufacturers in lowering the operating pressures (and, thus, costs) of these membranes. Significantly lower operating costs for EWP should be considered possible but not likely. Nevertheless, the system offers the potential of becoming more cost-effective than reverse osmosis for desalination of brackish water and treatment of wastes with high levels of total dissolved solids.

Recommendations for the California Energy Commission

Capacitive deionization is a promising technology but significant development is needed before it can be widely used in desalting applications. As a water-short state faced with a burgeoning population and static water supplies, California planners must consider desalting options. This technology could make desalting brackish water or sea water considerably more economical. However, to make it a viable option, additional research is needed.

The California Energy Commission should consider additional funding in this research area, particularly with pilot-scale demonstrations of the technology. Currently, there is limited pilot-scale data and most of the efforts have been done in the laboratory. The U.S. Bureau of Reclamation considers this technology the most promising new development in the field of desalting in existence today, and is considering funding a demonstration. The California Energy

Commission might consider participating in this study. CEC efforts should focus on energy use characteristics of the system, particularly in the area of energy recovery systems, where the CEC has extensive experience.

Electron Beam Irradiation

Background

Irradiation of aqueous solutions with high energy electrons results in the rapid formation of excited state species and free radicals. The free radicals generated will oxidize or reduce the organic and inorganic compounds present in the water, resulting in the formation of carbon dioxide, water and inorganic salts as the end product.

Electron beam was first applied to environmental processes in the late 1980s as a technology to clean up groundwater contaminated with organics. It is attractive because, like ozone, it is a significant initiator of oxidative reactions and generates no residual chemicals or solids. Research beginning in the early 1990s sponsored by EPRI assessed the potential for its use in disinfection of wastewater, and subsequently during the processing of meat. If commercially viable, electron beam irradiation could be used to treat industrial wastewater, render hazardous materials less so, and disinfect potable water supplies.

In order to become commercially viable, however, the costs associated with using the technology must drop significantly. Electron beam generation is an expensive process. The process uses accelerators which require substantial quantities of electrical energy to generate enough electrons to impart the energy into the irradiated material. The potential and problems associated with this technology are discussed in more detail below.

Theory & Operation

The radiation chemistry of water has been studied extensively. It is generally accepted that the introduction of an electron beam into water results in the generation of hydroxyl and hydrogen radicals, excited electrons, hydrogen peroxide and hydrogen gas. The amount of energy absorbed by irradiated material per unit mass is the dose, and a common unit used is a rad. One rad is the energy absorption of 100 ergs per gram of material. Studies show that maximum energy transfer occurs at approximately one-third to one-half of the maximum depth of penetration. The maximum depth is directly proportional to the energy of the incident electrons and inversely proportional to the density of the material being irradiated. In practice, the maximum depth of penetration for electron beams in water is quite small: only up to about 10 mm using commercially available electron beam accelerators. This presents challenges when using electron beam to treat large, full-scale quantities.

The electrons are generated in accelerators using electric current applied to a cathode. Once generated, the electrons are accelerated down a high-vacuum tube using very high voltages to achieve electron velocities around 96 percent of the speed of light. The speed and density of the electron stream are controlled by varying the voltage at the end of the vacuum tube and the

current applied to the cathode. The narrow, concentrated beam is spread out to a rectangular shape by a magnetic field at the exit of the vacuum tube. Electron penetration varies depending on current used: at 1.5 million volts at the end of the tube and 50 milliamps applied to the cathode, the electron beam will penetrate about 7 mm of water. Currently, system efficiencies, which is the amount of electric energy effectively imparted into the water stream, hover between 35 and 50 percent. According to industrial experts, these efficiencies would have to be improved by about 50 percent in order to make the process economic.

Electron beams produce both oxidative and reductive species, so irradiated water will have both oxidation and reduction reactions. This is one of the system's advantages compared to the more conventional process of ozone, which is principally limited to oxidation. Thus, it can be used to remove a wide variety of toxic organic compounds, as demonstrated by Cooper et. al. (1992). It is not suitable for metals or more common water treatment pollutants, such as suspended solids.

Past Research

Industry has recognized the many possible uses for electron beam processes from the plastics and rubber industry which use electron beams to enhance the material properties of their products, to the beams to enhance the material properties of their products, to the medical industry which uses electron beams to sterilize products, current research shows that electron beams can break down organic pollutants into a simpler compounds which are non-toxic (EPRI, 1992a).

Irradiation has been used commercially in the food processing industry since the early 1960s; however, it is only in recent years that food processors began using electron beam accelerators in lieu of cobalt irradiation. EPRI (1999a) lists a number of commercial vendors of electron beam accelerators supplying to the food processing market. The report indicates that commercial accelerators achieve much higher electrical efficiencies than the ones used for research purposes in the early 1990s (ranging from 70 to 85 percent). According to the study, the most significant benefit of using electron beam is that the process does not require radioactive material and thus is generally considered "cleaner" by the general public.

The EPRI MWW Program sponsored a bench-scale assessment of electron beam disinfection of wastewater at the Palo Alto Regional Water Quality Control Plant (EPRI, 1992b). This study identified the need to apply the electron beam to a thin film. Further, the study verified that an electron beam can disinfect filtered effluent from a wastewater treatment plant. The beam provided a 5 log reduction in total coliform at the highest dosage. In order to achieve these results very high specific energy was required. The researchers assumed that this was more a function of the application method rather than inherent economic inefficiencies with the electron beam process.

The EPA's Office of Research and Development conducted an evaluation of one vendor's electron beam technology to mineralize several chlorinated organics in a contaminated groundwater (EPA, 1997). The EPA found that the process could achieve better than 99 percent reduction of tricholoroethylene and perchloroethylene and over 90 percent reduction of 1,2-dichloroethylene. Initial concentrations ranged between 11,000 and 27,000 micrograms per liter. However, the EPA determined that mineralization was not complete in all cases and that the process did lead to the generation of limited amounts of ketones and aldehydes.

The New York Power Authority and EPRI cosponsored a study of disinfection options, including electron beam, to disinfect combined sewer overflows. New York City is currently implementing controls for combined sewer overflows and is reviewing a number of methods to disinfect these discharges, which occur during periods of heavy rainfall when the City's sewer system is overwhelmed by runoff. The study compared ozone, chlorine, electron beam and ultraviolet irradiation to disinfect the discharges. The researchers found that electron beam disinfection consumed considerably more power than any other alternative, in part because of problems the researchers had in developing useable dose-response relationships (Camp, Dresser & McKee, 1998). The system achieved limited disinfection but did not achieve the study goal of a 4-log reduction in certain target bacteria. The researchers concluded that the system was not optimized prior to the pilot tests and that this could account for the poor performance. However, it is likely that in order to achieve the disinfection goal even higher power levels were required.

More recently, researchers are assessing the synergistic effects of using electron beam with other technologies, such as ozone or UV. In addition, the researchers are using certain inexpensive additives which may enhance the effects of the electron beams. Initial experiments were not encouraging, however, because these chemicals (e.g. acetic acid) are needed in such high concentrations that it makes the process uneconomical (R. Curry, 1999).

Costs

There are little data available on costs for electron beam irradiation, but all estimators agree that the costs are highly variable and dependent on a number of factors, including dose, throughput or volume of waste, size of the treatment facility, and the time utilization of the facility. Electron beam irradiation becomes more economical with higher throughputs. EPRI (1999a) cited a study comparing cobalt irradiation and electron beam for food processing which found the costs to be similar for both processes. These costs ranged from $ 0.005 to $ 0.07 per pound of food material irradiated.

Gathering costs for environmental applications has been even more difficult. For instance, under the parameters defined in the CDM study discussed above, the electron beam process was rejected before cost estimates were made. Preliminary estimates by one vendor of equipment put the cost for the technology at between $0.50 and $ 2.00 per 1000 gallons, which is a very competitive price.

Perhaps the best estimates were made by the EPA during their technology evaluation in 1997 discussed above. The EPA (1997) estimated a treatment cost of $ 5.99 per 1000 gallons for a groundwater containing both aromatic and refractory organic compounds (i.e. a moderately-difficult-to-treat water). This estimate was based on a 21 kW system, which would be capable of treating a waste stream of 20 gpm. Interestingly, utilities represented about one-third of direct costs. The treatment cost was based on a 20 year amortization of the treatment unit. Costs were also developed from systems using large accelerators, including 45 kW and 75 kW. These costs are significantly greater than conventional methods of dealing with groundwater contaminated by chlorinated organics, such as activated carbon absorption. However, they more favorably compare with other oxidative-based technologies, such as ozone and hydrogen peroxide.

With continued improvements in accelerator efficiency, it is quite possible that unit costs will drop in the future. Electron beam irradiation has found commercial applications in a wide variety of material handling applications, so there is interest across a wide spectrum of industries to develop more energy efficient systems.

Recommendations to the California Energy Commission

Unlike many of the other technologies discussed in this section, electron beam irradiation is very close to widespread commercialization. However, it is finding considerable favor with food processors and it is in that industry where it will first grow. It is very likely that more energy efficient electron beam accelerators will be developed as the market for them in various industries continues to grow, but this will take some time. Thus, it would be unnecessary for the California Energy Commission to commit money to improving the economics of electron beam systems.

However, there have been very little demonstrations of the process for environmental applications. The EPA demonstration showed that these systems are complex and prone to breakdowns. While the researchers were able to complete the test protocol, they ran into continual problems. Further, large applications would require sizeable shielding of the accelerator to minimize workers' exposure to harmful effects. The track record to date of this process is decidedly mixed, and it is unlikely in the short term that electron beam irradiation will grab a significant portion of the environmental industry.

The California Energy Commission should continue to monitor this technology but additional funding of demonstration projects at this time is discouraged. With proven, more economical accelerators introduced into the marketplace it would become valuable to sponsor a demonstration of the technology. The most likely target for demonstration should be wastes that are costly to dispose of or treat, such as high-strength hazardous waste.

On the other hand, the California Energy Commission might consider sponsoring the use of the technology in food handling applications. Electron beam systems lend themselves to mobile units, so they could possibly be used as a central produce collection point in the Central Valley. While not quite an environmental application, the issue of food safety continues to grow today and makes a worthy target.

Supercritical Water Oxidation

Background

Synthetic organic compounds, widely used by a variety of U.S. industries, present one of the most challenging of waste disposal issues. These man-made, recalcitrant compounds can be very difficult to remove from the environment. Given that even low concentrations of synthetic organic compounds can present a threat to human health and the environment, their removal and destruction is imperative in many environmental applications.

Incineration and oxidation remain the most common methods used to treat synthetic organic wastes. However, the combustion or oxidation products that result from these treatment methods can be more hazardous pollutants than the original pollutant itself. Thus, an ideal treatment technology would ensure that the final products from converting these organic compounds were also harmless. One promising technology, capable of oxidizing synthetic organics to harmless organic salts, carbon dioxide and water, is supercritical water oxidation (SCWO).

Supercritical water oxidation has the potential to be a commercially-viable alternative for industry to eliminate the more difficult of synthetic organic wastes. However, it faces several engineering challenges to ensure that a system using this technology would be widely implemented by appropriate industries.

Theory & Operation

Supercritical water oxidation is based on the unique properties that water exhibits above its critical temperature of 374°C and critical pressure of 22.1 MPa. At these conditions, water acts as both a liquid and a gas. For instance, the density falls from 0.7 g/ml to 0.2 g/ml and, as there is little residual hydrogen bonding, the dielectric constant also decreases. Given these properties, supercritical water is a strong solvent of organic compounds, but a relatively poor solvent of organic salts. Organic matter and gases, including oxygen, are miscible with supercritical water. A process schematic is shown in Figure 4-3.

The poor solvency of organic salts leads to the development of brine within the system reactor. Thus, provisions must be made for the periodic removal of these salts during processing. In addition, salts can lead to corrosion problems; operating supercritical water oxidation systems have been plagued by severe corrosion, but recent advances by material scientists suggest that promising improvements are possible.

The process flow diagram in Figure 4-4 includes an oxidant delivery system, a fuel and waste delivery system, a preheater, a reactor, and a cooling and pressure letdown system. Effluent from the pressure letdown system passes through a gas/liquid separator and these streams are treated separately prior to discharge. The waste, fuel, and water are combined, pressurized, and pumped into a preheater. The preheater uses waste heat from the reactor to bring the mixture closer to the critical temperature of water. Oxidation reactions predominate in a supercritical water oxidation reactor, so air or oxygen is pumped into the mixture to achieve proper stoichiometric proportions.

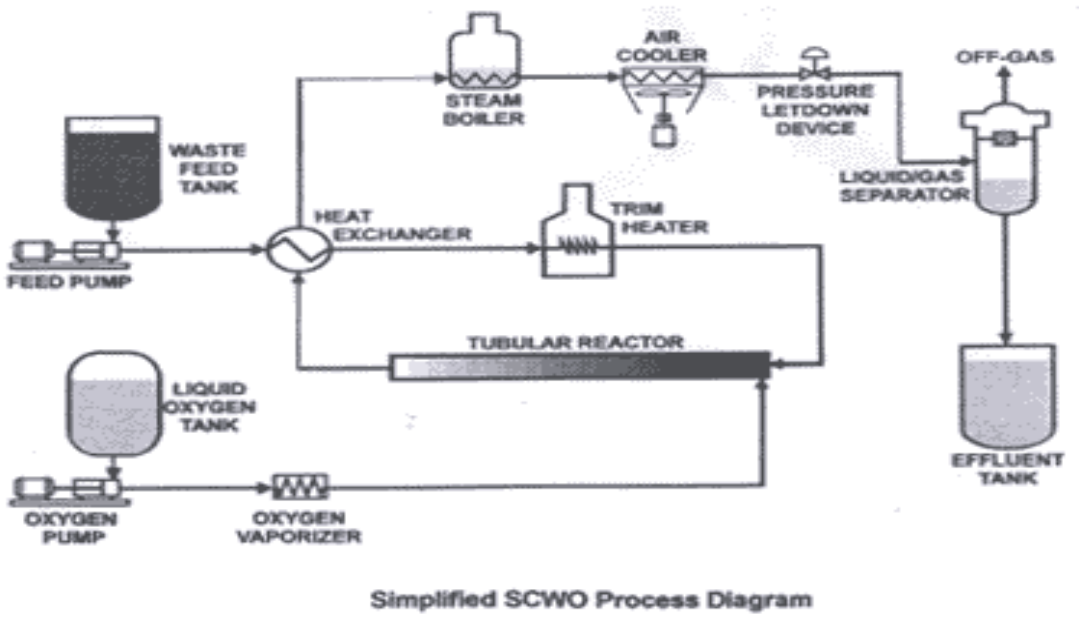

Figure 4-4
A Simplified Supercritical Water Oxidation Process Diagram

Once the mixture is preheated it passes into the reactor where the preheated stream mixes with the hot reactor contents. Exothermic (i.e. heat-releasing) reactions are initiated in the reactor, so temperature control is a key component of any operating system. The heat in the reactor can be controlled by the preheater temperature, but provisions are necessary to allow feed and oxygen flows to be immediately shut off should dangerously high temperatures be reached.

Depending on the waste stream, the exothermic reactions can release enough energy to make the process self-sustaining so that fuel sources can be stopped, which can greatly improve the economics. Further, the heat of the mixture discharged from the reactor can be used to preheat the incoming mixes, which also improves the economics.

In general, destruction efficiencies increase with increasing operating temperature, residence time, and pressure. Higher temperatures minimize the required residence time, while temperatures closer to the critical point minimize the problems associated with salt plugging. Furthermore, the density of the reaction medium is much higher at low temperatures, so smaller reactors operating at low temperatures provide residence times equivalent to those of large reactors at higher temperatures. The advantages of low temperature supercritical water oxidation operation can be utilized using catalysts, such as NaCl or HCl, to increase reaction rates. Operation at lower temperatures also reduces NO_x formation.

Reactor design represents one of the chief challenges in commercializing supercritical water oxidation. The ideal reactor material would be inexpensive, yet suitable for operation under high temperatures and pressures in a very corrosive environment. Current materials used include nickel alloys, cobalt alloys, refractory metals, ceramics and polymers. Recent advancements in the latter two materials show promise, but more research is needed.

A commercially viable supercritical water oxidation system should include heat recovery equipment (to improve process economics), a means to reduce pressure and cool the effluent, and equipment to polish the effluent. Heat from the reactor can be used to preheat the waste stream, improving the process economics. In addition, the effluent often contains heavy metals and brine; these contaminants can be removed from the stream using a conventional membrane system or ion exchange equipment.

Past Research

Supercritical water oxidation has been an emerging waste treatment technology for the past 15 years. There have been at least 15 patents issued in the United States related to supercritical water oxidation since 1981. The majority of the research in the U.S. into this technology has been sponsored by the federal government, principally to deal with radioactive and hazardous wastes.

Johanson et al. (2001) summarizes the work done by the Department of Energy's Hydrogen Program to use supercritical water partial oxidation (SWPO) of biomass and municipal solid waste to generate hydrogen. The research effort is being carried out cooperatively with General Atomics at their supercritical water pilot plant in San Diego, CA. The work is based on the theoretical computation that an aqueous mixture containing 11 weight percent wood will produce a dry gas containing 94 percent hydrogen (with the remainder composed principally of carbon dioxide). This theoretical assessment raises several practical questions, including: 1) what is the fate of fuel-bound hydrogen during partial oxidation; 2) how does the actual yield compares to the theoretical yield; and 3) is excess char produced with the effect of reducing the usable yield. The researchers intend to process ethanol, cornstarch, raw compost, bituminous coal, and a mixture of these feedstocks to determine the most appropriate manner to generate hydrogen.

There is little published information in the literature concerning SWPO. However, there have been a number of waste streams tested using supercritical water oxidation, including pig manure (Rulkens, et. al., 1989), pulp mill sludge (Modell, 1990), pulverized wood mixed with plastic, rubber and charcoal (General Atomics, 1999), and fermentation waste (Johnson et. al., 1998).

General Atomics has also conducted SCWO tests on sewage sludge. The process produces a solid byproduct consisting primarily of metal oxides. Organic destruction efficiencies exceeded 99% percent and both SO_x and NO_x concentrations were below the detection limit.

Mitsubishi Heavy Industries successfully demonstrated an alternative SCWO technology in a pilot plant using a proprietary technology for the destruction of PCBs developed by the SRI International of Menlo Park, California. By heating PCBs in water to 380 ºC at 270 atmospheres and introducing certain inexpensive catalysts, harmful chlorine was recovered as sodium chloride and organic carbon was converted to carbon dioxide and water.

Shaw (2000) presents an overview of current SCWO technology to treat wastestreams containing toxic military materials. Three types of reactors are currently in use, including tube

reactors, vertical downflow reactors, and transpiring wall reactors. Los Alamos National Laboratory has developed a tube reactor, which operates at low temperature (440°C) but high pressure (1070 atm), to destroy explosives. The U.S. Air Force is currently assessing a vertical down-flow reactor to treat various wastes from aircraft maintenance. In addition, the U.S. Navy is assessing a transpiring wall reactor for shipboard wastes. Clearly, the Department of Defense is currently funding the bulk of current research into SCWO as an environmental tool.

Private research efforts and uses of the technology are of considerably smaller scale than those of the federal government. A Texas chemical company currently uses the technology to treat waste amines and alcohols. Another Texas company is reported to be developing a system for treating municipal wastewater sludge. On the other hand, commercial development in Europe is more active, and includes work in Germany, France, Switzerland and Spain. Shaw notes that considerable complexity lies around phase separation in supercritical water solutions. Thus, a group of experts in solution thermodynamics, phase behavior, and aqueous solution properties met to develop guidelines for phase separation for supercritical water solutions.

Costs

Frisch (1998) gives the most complete estimate of anticipated costs for this technology. Basing his estimate on a hypothetical plant capable of treating 15 lpm (4 gpm) of a waste stream containing approximately 10 % organic content by weight, capital costs would be $ 2,823,000 and annual operating and maintenance costs would be $ $358,000. Of the operating costs, labor accounts for 36% percent of costs and liquid oxygen accounts for another 36% percent. These costs translate into a range of $0.053 to $0.079 per liter ($ 0.20 to $ 0.30 per gallon). The Texas company currently using a full-scale supercritical water oxidation system has calculated its costs as $ 0.37 per gallon, so the range seems reasonable. Further, these costs compare favorably with at least one conventional alternative. Off-site incineration costs range between $ 0.80 and $ 1.00 per gallon, suggesting that supercritical water oxidation could be cost-competitive.

Table 4-2 summarizes the costs of a supercritical water oxidation unit developed by EPRI (1995) for a hypothetical waste containing 10% percent organic waste

Table 4-2
Comparison of Costs for Hypothetical Supercritical Water Oxidation Plant Treating 5 and 20 Tons of Waste Per Day

Item	5 tpd unit	20 tpd
Capital Costs		
Installed Cost	$ 4,066,509	$ 12,535,805
Annual Recovery	$406,651	$1,253,580
Operating Costs		
Direct Labor ($ 20/hr)	$ 262,800	$ 262,800
Oxygen & Equipment Lease	$ 200,316	$ 729,263
Power ($ 0.07 per kWh)	$19,974	$ 79,652
Natural Gas ($ 2.50 per Mgal)	$69,779	$ 279,118
Cooling Water ($0.08 per gal)	$ 6,988	$ 27,951
Chemicals	$ 9,000	$ 18,000
Laboratory Services	$ 26,000	$ 52,000
Maintenance	$ 243,991	$ 752,148
Annual Tons of Ash Disposed (bone dry)	365	1460
Solids Disposal ($150/ton)	$ 136,875	$ 547,500
Total Annual Operating Costs	**$ 975,662**	**$ 2,748,432**
Credits (from steam production)	($13,000)	($ 53,000)
Net Cost (on a per gallon basis)	$ 0.313	$ 0.225

tpd = tons of waste processed per day

The data in the table above is instructive, in that it hints at the complexity of a SCWO unit. The unit requires a variety of inputs and maintenance costs are second only to labor costs in operating expenses.

Research Needs

The cost numbers assume a ten-year lifespan on any SCWO system. However, that length for useful equipment life may prove to be excessively optimistic. Corrosion is proving to be the most significant obstacle toward more widespread use of this technology. The National Association of Corrosion Engineers (NACE International) recently discussed the corrosion issue as it relates to supercritical water oxidation in their June 2001 edition of their newsmagazine.

Currently, technology developers are focusing on alloys of nickel or titanium. While these are providing good performance, there have been examples of severe corrosion. Certain types of stainless steel also perform well but can be susceptible to stress corrosion cracking. To address problems with corrosion rates in the temperature transition section of the reactors (a particular problem for nickel and titanium alloys), gold or platinum plating is being advocated by some.

Researchers at Pennsylvania State University are addressing these concerns using a different approach. Corrosion rates can be controlled by adjusting the pH in the reactor using certain chemicals, so the effort focuses on developing pH monitors capable of operating in the harsh environment of a SCWO reactor.

Gloyna and Li (1995) agree with this prognosis. The researcher were funded by a grant from EPA's National Risk Management Research Laboratory to assess the ability of SCWO to treat wastes containing EPA priority pollutants. The researchers found that SCWO systems can achieve greater than 99.99% percent destruction efficiencies in a totally enclosed facility. The study assessed reaction kinetics under both batch and continuous flow conditions. After quantifying the excellent performance possible for SCWO, the researchers focused on an engineering evaluation, which included an assessment of the material performance and chromium speciation. Different operating conditions led to different corrosion rates and destruction efficiencies, so there is a need to tailor the process to the specific waste stream. Currently, this can only be done empirically. They concluded that the process is understood and the potential is immense, but further emphasis is needed on technical aspects of process design and commercial-scale development.

Recommendations to the California Energy Commission

Supercritical water oxidation could find widespread application in the processing of a number of waste streams, including:

- industrial wastewater;
- industrial and municipal sludge treatment;
- mixed waste treatment;
- Department of Defense hazardous waste treatment;
- recovery of potable water during space travel;
- gaseous emissions (particularly VOCs).

It would compete against conventional disposal techniques like deep well injection and incineration. Particularly with challenging disposal problems like the mixed waste produced by nuclear facilities (i.e. wastes containing both radioactive and non-radioactive hazardous materials), it could prove superior to incineration. Highly radioactive wastes will be vitrified before disposal, but some of the contaminants present make this option less attractive. In addition, incineration leads to gaseous emissions, such as NO_x, that often must be further treated. Thus, supercritical water oxidation, which produces minimal NO_x and can achieve better than 99% percent destruction efficiencies, is a likely candidate technology for these hard-to-treat wastes.

In spite of these advantages, supercritical water oxidation has not attained widespread commercial success. One of the principal reasons behind this failure is that, under most circumstances, the destruction efficiencies attainable by this technology are simply higher than that required. In most environmental applications, there is no need to achieve greater than 99% percent destruction efficiencies. These high efficiencies come at the price of high operating costs, as bringing a waste up to the pressures and temperatures needed to achieve supercritical water oxidation requires a significant input of energy (at least to get started). Further, equipment failure due to corrosion is an inevitable consequence of operating at these high temperatures and pressures.

Given this dilemma, it is recommended that the California Energy Commission consider funding demonstrations of unique applications along with any developmental work to address the corrosion issues. For instance, assessments of a new reactor that could extend the life of a SCWO unit would be an appropriate use of research funding.

Advanced Oxidation Process using Nb-doped Titanium Dioxide Electrodes

Background

Conventional advanced oxidation processes (AOPs) are extremely effective at oxidizing organic compounds, particularly recalcitrant, or hard-to-treat ones. However, conventional AOPs are relatively energy inefficient. In general, these processes are generated using either ozone or ultraviolet light along with an initiator of some sort to convert the oxygen or ozone generated by this process into hydroxyl radicals. While effective for their intended use, these processes consume significant quantities of energy.

Alternative means of generating hydroxyl radicals have been the focus of much past research. The hydroxyl radicals can be generated chemically by combining ozone with a variety of initiators, including hydrogen peroxide, UV light, titanium dioxide (TiO_2), Fenton's reagent, and even a high pH. Hydroxyl radicals can also be generated via photocatalysis using UV light along with TiO_2 or Fenton's reagent. More recently, there have been attempts to use electron beams, plasma technology, sonolysis and gamma irradiation to generate hydroxyl radicals. However, in all of these cases moderate to significant energy is necessary. An AOP using niobium (Nb) doped titanium dioxide (TiO_2) electrodes is a particular application that offers the promise to greatly reduce the amount of energy needed to generate hydroxyl radicals.

Theory

The anodes consist of a Ti-metal substrate with an oxide coating comprising TiO_2 doped with 4 mole percent niobium (Nb) or tantalum (Ta) in the +4 valence state. The oxide coating is a heavily n-doped semiconductor, and the resulting electrodes have excellent corrosion resistance at the high potential needed to generate hydroxyl radicals. Under this setup, the efficiency of hydroxyl radical generation is almost an order of magnitude higher than in standard ozonators which are used in commercial and domestic water treatment applications. This technology may prove to be an economical alternative to ozonolysis.

The electron transfer process occurs at the surface of the semiconductor anode. This process is fundamentally similar to electron transfer occurring during photooxidation on TiO_2 surfaces. A positive space charge forms just inside the metal oxide layer at its interface with the electrolyte when a large positive electrode potential is applied to the anode (with an electric charge). This results in pronounced bending of the electron bands. When the doped conduction band inside the metal oxide lines up with the potential of the water/hydroxyl radical couple, electrons tunnel into the conduction band, converting water molecules at the surface of the metal oxide to hydroxyl free radicals which remain bound at the oxide/electrolyte interface. The surface bound hydroxyls react with substrate molecules at the surface of the anode. Because electrons are removed from the interface, recombination is not an issue, and quite large current efficiencies are observed: up to 90% in laboratory test cells, and 25 to 35% in larger prototypes that that have been tested in industrial settings. (The large difference in efficiency between the test cells and prototypes is due to the differences in the radius of the electrodes; narrower, laboratory-scale electrodes generate more hydroxyl radicals per unit power input but are impractical for industrial applications. Nevertheless, the efficiencies observed in the large prototypes are about twice those obtained by existing commercial ozone generators.)

The electrodes are produced by baking a coat of TiO_2 doped with niobium on to a titanium-metal substrate under conditions that favor the +4 oxidation state of niobium. Methods have been developed to produce rod electrodes and disk electrodes for laboratory use. Subsequent improvements have allowed production of plate electrodes of titanium-sheet and porous electrodes of titanium-fiber.

Porous anodes are produced by coating bundles of 50μm diameter Ti fibers with the same metal-doping composition. The time needed for water to flow past a fiber is only 0.5 ms, and the thickness of the diffusive boundary layer formed is on the order of 1 μm, allowing excellent mass transfer.

This process is expected to find applications for destroying chemical and biological contaminants at levels much greater than other advanced oxidation processes can handle at reasonable costs. Potential uses include any application utilizing hydroxyl ion oxidation, such as industrial wastewater control, groundwater remediation, gaseous emission control, and treatment of landfill leachate.

Characteristics of Niobium

Niobium is a transitional metal with an atomic number of 41 and an atomic weight of 92.9. It is a rare, soft, malleable, ductile gray-white metal. According to the Tantalum-Niobium International Study Center in Brussels (www.tanb.org), about 90 percent of current niobium usage is in structural steels, heat resisting steels, and superalloys that are iron, nickel and cobalt based. It is also used in high refractive index glass as found in piezoelectric devices and as an alloying addition to zirconium for nuclear reactor fuel tubes. There is more recent interest in niobium from the computing industry as a replacement for a related element, tantalum, which is used in capacitors. One of its more interesting potential applications in a pure form is in superconducting cables, a cross-section of which is shown in Figure 4-5.

A small portion of the niobium used today is recovered from tin slags and columbite/tantalite minerals, which are the source of much of the world's tantalum. Most of the world's niobium is recovered from ferroniobium, which is a byproduct of the smelting of the mineral pyrochlore, a calcium fluniobate. Two mines in Brazil account for 80 percent of the world's niobium and one in Canada accounts for more than half of the remainder. The pure chemical and its oxide are extracted from their ores after concentration by chemical treatment. A hydrofluoric acid-sulfuric acid mixture is used to bring the niobium compounds into solution. This solution is mixed with methyl-ethyl-ketone, which dissolves the niobium into the ketone while the impurities remain in the aqueous solution. The organic and inorganic mixtures divide into different layers and are separated using conventional liquid-liquid separation techniques.

Figure 4-5
Cross Section of a Superconducting Cable Made of a Niobium-Tantalum Alloy

The U.S. imported about 6,500 metric tons of niobium-containing compounds, including mineral concentrates, metals and alloys, niobium oxide, and ferroniobium. Prices from 1996 to 1999 averaged about $ 3.00 per pound but that price recently rose to $ 6.25 per pound due to the increase in demand. That demand is expected to grow at the same rate as its principal use in the steel industry.

Previous Research

There has been substantial work on advanced oxidation processes to address vexing environmental issues. Rice (EPRI, 1996) describes the chemistry behind advanced oxidation processes in detail. The term was coined by Glaze et al. (1987) to describe processes that produced the hydroxyl radical, HO. Some of the more common ways include:

- Ozone at elevated pH;
- Ozone plus UV;
- Ozone plus hydrogen peroxide;
- Ozone plus Fenton's reagent;
- UV plus hydrogen peroxide;
- Ultrasonic;
- Pulsed corona discharges;
- Supercritical water oxidation;
- Ozone plus electron beam irradiation.

The list above is not all inclusive: there are numerous ways to generate this highly reactive species. However, only those involving ozone, UV and hydrogen peroxide have attained the most commercial status.

Once generated, the hydroxyl radical has proven very effective at initiating a variety of oxidation reactions with other compounds. Thus, the hydroxyl radical can be used to oxidize many of the more recalcitrant organic compounds found in wastewater and air from modern industrial processes. There are numerous instances in the literature where advanced oxidation processes have been used to treat a variety of industrial wastewater. Hoefl et al. (2000) compared three different advanced oxidation processes on pharmaceutical wastewater to remove assimable organic halides (AOX) and chemical oxygen demand (COD). The researchers found that all three methods were capable of removing the targeted pollutants. Ledakowich and Solecka (2000) noted an improvement in the biodegradation kinetics of wastewater from a textile mill after treatment using advanced oxidation processes. Brillas et al. (2000) mineralized 2,4-D (a pesticide now banned by the U.S. EPA) using a mixture of hydrogen peroxide and iron (II). Arslan et al. (2000) decolorized textile effluents using ozone plus Fenton's reagent and ozone plus hydrogen peroxide. It is quickly apparent from a perusal of the literature that advanced oxidation processes may prove suitable for a large variety of applications.

EPRI (1996) notes that of all the processes listed above, only those involving ozone, UV and Fenton's reagent have currently achieved the most commercial status. At this time, for many industrial applications there appear to be no inexpensive means of generating hydroxyl radicals in concentrations sufficient for use. There is a need for more inexpensive ways of producing these compounds, which is the chief attraction of Nb-doped TiO_2 electrodes into this particular assessment.

There has been some research into the physical characteristics of titanium dioxide (TiO_2) electrodes. Graves et al. (1992) assessed the electrochemistry of magneli phase titanium oxide ceramic electrodes for the generation of ozone. The researchers found that if the electrodes are plated with lead dioxide, the electrodes will produce ozone when an electric current is placed between them. Peill and Hoffmann (1996) used a novel optical fiber cable reactor to deliver UV light to solid-supported TiO_2 with the intent of initiating advanced oxidation processes in contaminated wastewater. The system was effective in the photodegradation of pentachlorophenol, 4-chlorophenol, dichloracetate, and oxalate.

Kesselman et al. (1997) present a summary of laboratory attempts to generate hydroxyl radicals using Nb-doped TiO_2 electrodes. The chief advantage of this process is that it offers the potential to generate the large quantities of hydroxyl radicals needed to develop a commercially-viable waste treatment process. The researchers observed that electrode life was related to the operating current densities used during the experiments. Higher current densities lead to shorter electrode lives, pointing to a key question to be answered by any more detailed evaluations. Li et al. (2000) developed an innovative TiO_2 mesh to photooxidize wool dye and trichlorophenol.

Anticipated Costs

As mentioned above, the cost for niobium is projected to range upwards of $ 6.00 per pound. As a matter of reference, zinc prices range from $ 0.25 to $ 0.75 per pound while prices for gold have ranged from $ 260 to $ 400 per pound in the past ten years. Thus, niobium is an affordable metal that qualifies as a commodity (rather than a precious metal). Further, one of the principal advantages of TiO_2 is its low cost. Thus, this particular approach to generating hydroxyl radicals should prove to be cheaper than more conventional, commercially-available ways.

The Groundwater Remediation Technology Analysis Center published a summary of UV/oxidation treatment of groundwater (Trach, 1996), which stated that costs for this type of treatment of contaminated groundwater ranges from $ 0.10 to $ 10.00 per 1000 gallons, depending on targeted pollutants and the treatment goals. (The center is operated by Concurrent Technologies Corporation (CTC), in association with the University of Pittsburgh's Environmental Engineering Program, under a Cooperative Agreement with the U.S. EPA.) However, much of the literature shows a much that costs for advanced oxidation processes tend to be on the lower side of this range. For instance, the EPA (2000) conducted an analysis of using advanced oxidation processes to remove methyl tert butyl ether (MTBE) from a contaminated wellfield in Southern California. The pilot demonstration showed that ozone combined with granular activated carbon and absorption by a synthetic resin could lower MTBE concentrations from 80 ug/l to less than 3 ug/l for approximately $ $1.50 per 1000 gallons. Based on a preliminary review, the niobium-based technology would be competitive with any

conventional advanced oxidation process if it can generate sufficient concentrations of hydroxyl radicals to effect treatment.

Recommendations for the California Energy Commission

The developers of Nb-doped TiO_2 electrodes for AOPs propose to build and demonstrate prototype water treatment units in the range of 10 to 40 L/min flow capacity. They would be located at industrial sites for operational testing. The prototype units will operate at about 30% current efficiency and 6V cell voltage, corresponding to 67 kWh/kg of chemical oxygen demand destroyed. Research is needed to improve electrode life, current efficiency, and reaction kinetics at small concentrations of contaminant. At least a two-fold improvement in energy cost is expected as the electrodes and process conditions are optimized.

The initial assessments are promising, so it is recommended that the California Energy Commission consider funding a small demonstration project of the prototype unit under controlled conditions in the laboratory for a modest fee. If the prototype is successful, the Commission can consider a more detailed pilot demonstration at an industrial location. The bench-scale evaluation of the prototype could be limited to $ 50,000 or less, while a pilot demonstration should not exceed $ 200,000.

Freeze Conditioning

Sludge is a mixture of water and solids. Various industrial processes will produce sludge that, oftentimes, contain only small amounts of solids (less than five percent by weight). Thus, in disposing of contaminated sludge, there is a significant amount of resources expended in disposing of the water in the sludge. Technologies that can economically reduce the water content of sludge could become very beneficial.

Under current conditions, separating the solids from the water is not economical. However, as environmental regulations governing how and where to dispose of the sludge generated by industrial processing become more stringent, and as the value of water supplies grow, separation of the water will become more economically competitive. One very promising technology that is currently used on solid and water mixtures of high value (e.g. orange juice), freeze conditioning, could find many environmental applications.

Theory & Operation

Freeze conditioning competes against other water removal technologies, such as evaporation or membrane separation. In theory, freeze conditioning of sludge should be more energy efficient than competing, thermal-based technologies because the heat energy required to boil a given quantity of water is substantially greater than the energy needed to freeze an equal quantity. In practice, however, it has been a challenge to design a system capable of competing with membrane separation processes.

Industrial sludge contains several types of water: free water, interstitial water, surface water and water that is chemically-bound to solid particles. In sludge, surface water and free water freezes first. As this water freezes, ice crystals project from the frozen water towards the other types of

water. As the ice crystal growth continues, sludge solids are bypassed when crystals merge, and the solids are pushed from the ice lattice structure. Once all the free water is frozen, the interstitial water is extracted by diffusion. Based on previous research, it is unclear whether chemically-bound water is affected by freeze conditioning. However, qualitative assessments of sludge that has been freeze conditioned indicates that the nature of the material has changed.

Once the ice block is melted, the impurities can be easily separated from the water. This is accomplished by allowing the ice to melt, with or without crushing (to speed the melting process), and then passing the conditioned material through conventional dewatering equipment, such as belt filter press. In tests conducted by EPRI since 1996 on water treatment sludge, the freeze conditioning processes has proved very effective, particularly with sludge containing metal salts (such as alum), where much of the water is chemically bound to the solids.

The rate of freezing, concentration of sludge solids, and length of time the sludge is kept frozen before subsequent processing are the principal variables. An optimum freezing rate allows for complete dewatering of the solids in the sludge. If the rate is too fast, sludge solids are bound within the frozen block and not pushed towards the front of the ice front. Parker et. al. (1998) determined that an increase in freezing rate leads to poor dewaterability due to the fact that solids are entrapped as the ice front passes through the sludge. The authors also determined that the sludge should be kept below freezing for at least one hour to ensure that the mass is completely frozen. Operating at lower temperatures offers the added advantage of minimizing corrosion issues, so cheaper materials could be used for construction, than competing technologies, such as membranes.

There are several types of refrigeration systems available commercially that could be adopted for use with freeze conditioning, each with distinct advantages and disadvantages. Refrigerant systems can be either direct or indirect. In an indirect system the process mixture and refrigerant are physically separated. There is over 40 years of experience in using these types of systems in industrial processes. There are also three types of direct refrigerant systems, discussed below, where the refrigerant is mixed with the process stream.

Triple point systems simultaneously freeze and vaporize the process stream. Some of the fluid is vaporized, thereby removing heat from the system to cause ice to form. The mixture operates near its triple point. The vaporized stream is condensed using an absorbent loop or compressor. Direct-secondary systems use a separate, added refrigerant that is vaporized in the freezer compartment. The refrigerant must be recovered using wash columns, decanters and stripper columns, but much less material transfer occurs in these types of systems compared to direct-secondary systems.

The third type of direct refrigerant systems is the direct-calthrate system. In this system a refrigerant is also added, but the refrigerant forms crystals having two or more compounds. The refrigerant and solvent chemicals are joined physically but not chemically, so the solvent crystals are at a higher temperature than if the crystal consisted only of solvent. These systems can operate at ambient temperatures, but must deal with separating the process stream, refrigerant, and clathrated materials.

Current Research

The Electric Power Research Institute (1998) has operated a freeze/-thaw conditioning trailer since 1997. The trailer allows interested parties to investigate the possibility of using freeze conditioning on environmental sludge, such as those from water or wastewater treatment plants. To date, the system has been used predominately on water treatment plant residuals consisting of alum, water and the natural matter present in any raw water supply. The system uses an indirect refrigerating system with ammonia as the refrigerant. A schematic of the trailer is presented on Figure 4-6.

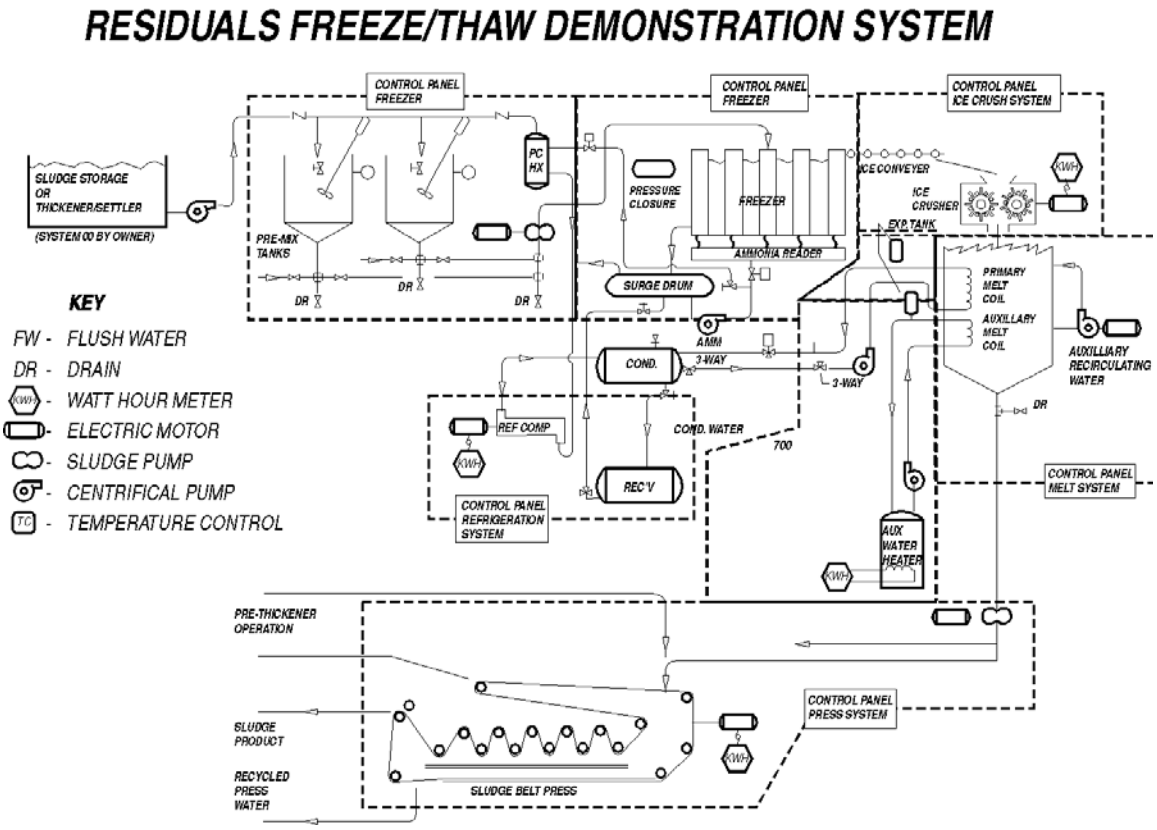

Figure 4-6
Schematic of Residuals Freeze/Thaw Demonstration System

Experience with freeze-drying of food products such as coffee has shown that the cost of freeze concentration will depend on the type and quantity of material involved. In environmental applications, particularly with industrial wastes, the intrinsically low value of the end product would allow the designer to choose a less robust system.

The capital costs for freeze concentration systems are high. Typically these costs are anywhere between 1.5 to 7 times higher than costs for a conventional evaporation system. Often the higher capital cost is due to the fact that most of these systems are custom built and designed. Cheremisinoff (1996) estimated that a ‘standard’ direct-secondary freeze/thaw conditioning

system producing 10 gpm of clean product water from a hazardous waste would cost between $ 1.0 and $ 1.5 million, assuming the unit was both mobile and highly automated.

Parker and Collins (2000) developed a cost model using cost data from several commercial ice makers. The authors assessed a number of different possible scenarios under which to assess the technology. Under one scenario where electricity costs were assumed to be $ 0.09 per kWh and tipping fees were approximately $ 75 per m^3, freeze/thaw conditioning could reduce disposal fees from $ 37,000 per year to approximately $ 11,000 per year. This savings more than offsets the capital and operating costs of the freeze/thaw equipment of approximately $ 15,000 per year. The authors developed a graph showing potential cost savings based on electricity costs and disposal costs. According to this analysis, the process can achieve better than 10% percent cost savings where disposal fees exceed $ 25 per m^3 and electricity costs exceed $ 0.03 per kWh.

A comparison of alternatives is also given by EPRI (1998). The alternatives included a standard belt filter press, freeze/ thaw without any preconditioning (i.e. treating sludge with a solids content of approximately 3% percent), and freeze/thaw of thickened sludge to 10% percent. The costs below were for a mythical water treatment plant using alum as a coagulant that produces an average of slightly more than 300,000 gallons of sludge per month. It was assumed that all treated sludge is shipped to a landfill for final disposal, where tipping fees are $ 80 per wet ton. The results are summarized in Table 4-3.

Table 4-3
Cost Comparison of Treatment Alternatives

Item	Belt filter Press[1] ($)	Freeze/thaw treatment of sludge[2] ($)	Freeze/thaw treatment of thickened sludge[3] ($)
Belt press	185,000	71,500	71,500
Fee pump & Polymer feed	70,000	70,000	70,000
Building	200,000	400,000	300,000
Crane	75,000	75,000	75,000
Cover Truck Loading	7,000	7,000	7,000
Conveyance Equipment	39,000	39,000	39,000
Freeze/Thaw Equipment	0	890,000	500,000
Subtotal	576,000	1,552,500	1,062,500
Site Work	30,000	60,000	45,000
Electrical & Instrumentation	90,900	108,400	91,100
Subtotal	**696,900**	**1,720,900**	**1,198,600**
Contractor General Requirements	104,500	258,100	179,800
Contingencies	160,300	395,800	275,700
Engineering	96,200	237,500	165,400
Total	**$ 1,057,900**	**$ 2,612,300**	**$ 1,819,500**

(1) Assumes thickened solids are pumped to a belt filter press for dewatering and disposal.

(2) Assumes solids are pumped to freeze/thaw conditioner, then to gravity thickener; thickener centrate is dewatered with belt filter press.

(3) Same assumption as (2) with additional preconditioning of gravity thickener prior to treatment in freeze/thaw conditioner.

Recommendations for the California Energy Commission

Freeze conditioning is an emerging but promising technique for reducing the quantity of industrial sludge incinerated or landfill in the state of California and throughout the United States each year. The volume of any sludge with a significant component of water could potentially be significantly reduced using freeze conditioning. Capital costs for installing equipment capable of conditioning industrial sludge could be a significant stumbling block towards more widespread use of this technology. However, the technological challenges associated with the development and refinement of suitable systems is not particularly large given the mature refrigeration industry currently in existence in the United States. Thus, given the right location, economical systems capable of competing with more conventional approaches to sludge management could be developed quickly.

A cursory economic analysis conducted by EPRI on freeze conditioning in the United States estimated that the process could be economically feasible in locations where tipping fees for landfilling sludge exceed $ 60 per ton and electricity costs were below $ 0.07 per kWh. However, this analysis was based on a hypothetical water treatment plant generating a benign sludge and without significant transportation costs. If the sludge must be trucked a large distance or tipping fees are significantly higher (as with hazardous sludge), the economic feasibility of freeze conditioning could be much greater.

The California Energy Commission could devote research to the development of freeze conditioning in two principal areas. The first would be in the development of full scale freeze equipment specifically designed to treat industrial and hazardous sludge. The high cost of disposing of this waste justifies the significantly higher cost of the freeze thaw equipment over more conventional processes, such as belt filter presses. The second focus should be on further refinement of freeze conditioning economics, particularly in those regions of the state with harsh winters where natural freezing processes could augment the mechanical process. This emphasis, coupled with strides made in the recent past in refrigeration equipment (such as ground-source heat pumps) could be incorporated into the system design to reduce costs.

The potential savings payoff associated with improving the energy efficiency of refrigeration equipment is large but a more risky venture. The CEC could consider requesting a royalty agreement with a product developer interested in building a commercially viable prototype. Based on prior history, demonstration studies could be conducted for between $ 50,000 and $ 200,000, depending on the project scope. Based on the potential payoff but higher risk of this research, it is recommended that the CEC give this research emphasis a lower priority than conducting studies on hazardous sludge.

Non-Thermal Plasma Destruction

Background

Non-Thermal Plasma (NTP) destruction is one type of AOP that results in the destruction of a wide variety of emissions, including NO_x, SO_2, VOCs, heavy metals and other toxic air pollutants. In essence, NTP technologies produce free radicals, and promote oxidation and molecular dissociation to enable enhanced chemical reactions that destroy hazardous emissions. NTP technologies differ from thermal plasma technologies in that the temperature of the bulk gas remains low for the NTP case, but is elevated for the thermal case. This is because energetic electrons are produced in NTPs without heating the entire gas stream to high temperatures. The plasmas produced by NTP processes are sometimes referred to as cold plasmas, because of this unique low-temperature property. Therefore, one advantage that NTP technologies have over thermal plasma discharge is that less energy is required for NTP processes to achieve the same degree of chemical reaction.

Theory and Operation

There are several main types of NTP reactor technologies, including electron beam, dielectric barrier discharge, pulsed corona discharge, and flow stabilized discharge. The technologies are similar in that they all generate energized electrons that collide with atoms and molecules in the contaminated gas and create highly reactive chemical species. The reactive species, in turn, react with pollutants in the gas and transform the pollutants into more controllable compounds. The general process for NTP destruction is depicted schematically in Figure 4-7.

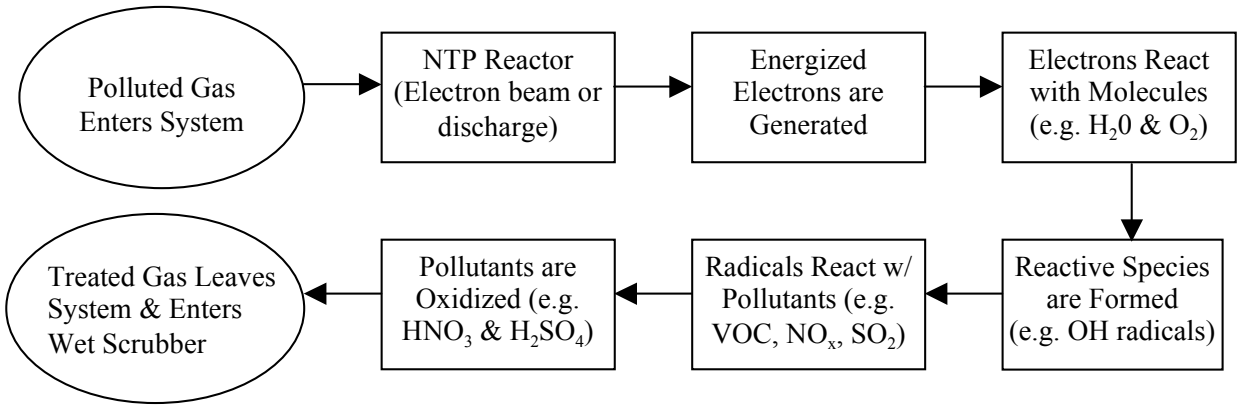

Figure 4-7
A Schematic Representation of the Non-Thermal Plasma Destruction Process

The differences between the technologies lie in the manner in which the energized electrons are generated and introduced to the gas stream. For the electron beam method, electrons are generated externally from the gas. For all of the discharge technologies, electrons are generated by discharge electrodes within the gas stream. The various discharge technologies vary in the

way they avoid arcs from forming across the electrodes. If the current is increased to high levels, the energy consumption increases, and the efficiency is reduced. Moreover, the plasma begins to change from non-thermal to thermal, whereby the background gas is energized along with the electrons.

One of the ways to produce NTP is with an electron beam. In this process, electrons are generated externally within a high vacuum environment, outside of the reactor. The electrons are then introduced to the gas stream through thin films (or, windows) of titanium or boron nitride, where they react with the gas and create NTP (Urashima and Chang, 2000).

Electron beam technology for NTP does not appear to be receiving much research emphasis when compared to other types of NTP technologies. This could be due in part to other technologies, such as dielectric barrier discharge and pulsed corona discharge (discussed below), being potentially more advantageous in terms of technical ease, scalability, and lower initial costs (Puchkarev et al.). There is also some indication that electron beam technology uses more energy to achieve the same level of destruction.

Dielectric barrier discharge is currently one of the main areas of focus in the NTP research arena. Dielectric barrier discharge reactors use high voltage discharge from electrodes to destroy gaseous contaminants. There are various types of dielectric barrier discharge reactors, including double dielectric barrier (or, silent) discharge, surface discharge, packed (or, pelletized) bed discharge, and trench discharge. The primary difference between the reactor types is the reactor geometry and the placement of the dielectric material. All dielectric barrier discharge technologies use a dielectric material as a barrier to prevent arcing or spark discharges between metal discharge electrodes. Arcing and spark discharges would increase the energy consumption greatly. The dielectric material is an insulating material with high dielectric strength, and a high dielectric constant. The electrodes are typically fed with an AC power supply in the 50 to 10,000 Hz range. As the AC voltage reaches its maximum, charges begin to accumulate in the dielectric material. Then, thin filament current pulses (or, microdischarges) are generated from the dielectric surface as the voltage polarity shifts (Urashima and Chang, 2000). The microdischarges are distributed within the gap between the discharge electrodes, and lead to the creation of a NTP environment that is effective for destroying gaseous contaminants. First, radicals are formed via collisions of electrons with molecules, such as water and oxygen. The radicals then oxidize pollutants to create less hazardous compounds. In particular, the reactions in the NTP destroy VOCs and convert SO_2, NO_x, and mercury (Hg) to more easily controlled chemical species (i.e., sulfuric acid, nitric acid, and mercuric acid) that can be removed subsequently with a wet scrubber.

Pulsed corona discharge is another category of NTP technology that has received considerable attention recently. In pulsed corona systems, a pulsed voltage is used to prevent the current from increasing to the point where spark discharges occur. The resulting environment is one that is analogous to the environment generated with dielectric barrier systems, in which micro- or streamer discharges are present. Two common types of pulsed corona discharge technologies include the wire-coaxial reactor and the wire-plate reactor.

In a pulsed corona reactor, the applied voltage is applied such that it is below the ion frequency. This enables the excitation of electrons without the excitation of heavier ions, and minimizes the energy input by avoiding the motion of heavy ions. For pulsed power systems, a traveling wave electric field can be induced to enhance electron excitation by use of a power supply that is able to generate a very large rate of current change in discharge. One limiting factor of pulsed technologies is scalability. This is because the impedance of electrode system and the size of the reactor are proportional (Urashima and Chang, 2000). This challenge can be dealt with by improving impedance matching, and with optimization of electrode design. As with other NTP technologies, the plasma that is formed in pulsed corona system leads to enhanced chemical reactions, and to the ultimate destruction of toxic compounds.

In flow stabilized discharge systems, the electrodes are continuously cooled by the rapid flow of gas that flows directly through the inside of the electrodes. This high flow-rate gas prevents the streamer discharges from becoming unstable. There are several systems with different types of geometries under investigation, including the corona torch, capillary tube, corona radical injection, and corona radical shower configurations. Typically, flow stabilized discharge is for degrading fairly stable gases (e.g., VOCs and Ozone Depleting Substances (ODSs)) (Urashima and Chang, 2000).

Current Research

Currently there is a considerable amount of research being conducted by government agencies, universities, and research institutes into air emission control with NTP destruction technologies. Table 4-4 shows a list of some of the recent research activities. The specific technologies under investigation vary from one organization to another, but have the common characteristic of using NTP to facilitate the destruction of dangerous pollutants. Researchers are experimenting with various reactor designs, and are studying critical parameters that affect destruction efficiencies. Research efforts have resulted in successful pilot and demonstration projects, and products and systems are beginning to emerge into the marketplace. For the most part, product development is in the early developmental stage.

As described above, the main NTP technologies include electron beam, dielectric barrier discharge, pulsed corona discharge, and flow stabilized discharge. In addition to these, there are several technologies that are based on variations to the traditional NTP processes. There are also hybrid processes that combine the benefits of NTP with those of another control technology. The technologies in these categories include pulsed dielectric barrier discharge, pulsed glow plasma chemical process, pulsed corona enhanced wESP, plasma/catalyst and plasma/adsorbent systems, and gliding arc discharge.

Most of the NTP technologies are still in the early stages of laboratory testing. However, at least four research groups were found that are either in the field demonstration stage, or have commercially available products for stationary emission control. Three of the groups are developing dielectric barrier discharge systems; the fourth is developing products based on the flow stabilized discharge technology. In all cases, the technologies are more mature for VOC destruction than for NO_x or SO_2 control.

It is not uncommon for NTP technologies to achieve VOC removal efficiencies of 99% for industrial applications. In addition, some NTP developers claim they will be able to achieve NO_x reductions of greater than 95% (EPA, 1999).

NTP technologies are also being developed for automobile emissions. Litex Corporation is developing a product called Litex CDD™ that is intended to be inserted into the exhaust stream of gasoline engines, upstream of the three-way catalytic converter (Litex). The product is based on corona discharge technology, and is thought to reduce CO emissions by more than 80% and NO_x emissions by more than 50%.

Table 4-4
Partial List of Current Research Efforts in the Non-Thermal Plasma Destruction Field

Technology	Research Group	Primary Targeted Applications
Dielectric Barrier Discharge	Ecozone Technologies, Ltd.	General Emissions Control, Vendor
	CSIRO Telecommunications & Industrial Physics	General Emissions Control and Surface Treatment
	Los Alamos National Laboratory	General Emissions Control
	NJIT	General Emissions Control
	Southern Illinois University	SO_2 and NO_x Control
	Illinois Clean Coal Institute	SO_2 and NO_x Control
	Pacific Northwest Laboratory	VOC and Soil Off-Gas Remediation
	EPA	VOC Control
	Tokyo Institute of Technology & Thammasat University Rangsit Campus	VOC Control
	Inha University & Belarus State University of Computer Science and Radioelectronics	VOC Control
Pulsed Corona Discharge	Florida State University	General Emissions Control
	Southwest Research Institute	General Emissions Control
	Lawrence Livermore National Laboratories	NO_x Control
	University of Southern California	Diesel Exhaust - NO_x Control
Flow Stabilized Discharge	PlasmaSol Corporation & Stevens Institute of Technology	General Emissions Control, Vendor
Pulsed Dielectric Barrier Discharge	University of Illinois	NO_x Control
Pulsed Glow Plasma Chemical	Oak Ridge National Laboratory	VOC Control
Pulsed Corona Enhanced wESP	University of Cincinnati	SO_2 and NO_x Control
Barrier Discharge with Catalyst	Siemens AG	Mobile NO_x Control
Corona Discharge with Catalyst	Environmental Elements Corporation & EPA	NO_x Control
	Litex Corporation	Mobile NO_x Control, Vendor
Gliding Arc Discharge	UIC	General Emissions Control
General NTP Research	McMaster University	VOC Control

Anticipated Costs

Cost data for NTP technologies are rather limited since products are only just beginning to emerge into the marketplace. In general, NTP technologies are considered to have moderate costs as compared to competing technologies. Ecozone estimates that the initial cost of its dielectric barrier discharge product called NT-PACT is around 30% lower than costs for incineration and catalytic oxidation products from competing vendors. They also claim that operating costs are lower, and their system is easier to operate (Ecozone, 2001).

Established, competitive technologies can effectively remove SO_2 and VOCs, but these are expensive and there is a continuing need to make environmental controls more cost effective. Absorbers effectively SO_2 and VOCs; however, these have moderate capital costs and high operating costs. Thermal oxidation methods, either using direct flame or catalysts require low capital investment but demand moderate to very high operating costs. Condensers have low operating costs but the capital expenses needed to install a system.

Additionally, the projected initial cost for a 105 scfm prototype field system developed by Pacific Northwest Laboratory for soil off-gas treatment is $50,000. However, with large-scale production, this cost is likely to be less. The system is also expected to require the labor equivalent of a one-quarter-time person. The total cost is projected to be around $10 per pound of contaminant ($0.35 of which is for the energy requirement). This cost includes a 25% contingency for unknown additional costs, and assumes 8% downtime. The capital payback period is assumed to be 6 months (EPA, FRTR).

For Litex's CDD™ system for automobile emission, the expected volume price is around $100, and power requirements are approximately 25 Watts.

Recommendations for the California Energy Commission

Because of its ability to destroy several categories of air pollutants simultaneously, effectively, and with moderate costs, NTP is a very promising solution for gaseous emission control. However, currently some NTP technologies seem to be limited in scalability, particularly for the destruction of NO_x from high gas flows. In addition, although many researchers claim that NTP technologies yield no undesirable byproducts, some suggest byproducts, such as dioxins and furans, may be generated during treatment of soil off-gas and then released into the atmosphere. Therefore, it is recommended that the CEC contribute to further research and development efforts aimed at scaling up NTP reactors, and better understanding the emissions NTP processes destroy, as well as potentially generate.

Selective Ion Exchange

Background

Ion exchange is a conventional pollution control process used in a variety of water and wastewater applications. At its simplest level, ion exchange involves passing the target fluid through a specially formulated solid media. As the water passes through the media, dissolved salts (ions) in the water are exchanged for benign ions (usually sodium) in the media. In this way, dissolved salts can be removed from the water stream. The water stream is continually passed over the media until all the exchange capacity of the media is exhausted. This is usually determined by measuring for the presence of the targeted pollutant in the ion exchange column effluent. Once this occurs (what is known as "breakthrough"), the media is regenerated by passing another chemical through the media to remove the pollutants collected and the restore the media to its original condition. The ion exchange media are either naturally occurring

inorganic zeolites or synthetically produced organic particles. The synthetically produced resins are favored today because they can be tailored for specific applications.

One of the most significant challenges in using ion exchange in the past has been that the media is typically not very selective. In the most commonly-used ion exchange media, all monovalent or divalent cations are removed, including both the targeted ones and more benign ones. The result is that the run time of the media (i.e. the time until the media is regenerated) is shortened when compared to the run time possible if only the targeted pollutant or pollutants were removed.

After nearly a decade of research effort, a California company is close to developing a selective ion exchange. The researchers claim they have accomplished this through a special formulation of the ion exchange media.

Theory & Operation

The process uses a ligand-based media to selectively recover toxic anions from aqueous solutions. The media is both highly selective and inexpensive. The closed loop system extracts the targeted contaminant by absorption into a non-soluble form. The media used is a ceramic powder with secure bulk supply and rapid adsorption kinetics. The loaded media has passed EPA TCLP testing.

The company claims that a simple caustic flush regenerates the media, and that they have provided more than 50 regenerations with no capacity loss. The company developed a proprietary electrochemical process to recover the contaminant in a benign insoluble form. The caustic based regenerant can be reused in the closed loop process, making the operation more economical.

A recent demonstration at a aircraft manufacturing plant in Southern California demonstrates that the system has promise. In the study, the selective ion exchange media proved capable of removing chromate (VI) from a 3 gallon per minute waste stream from an inlet concentration of 120 ppb to an outlet concentration under 2 ppb. Further, the process also reduced perchlorate concentrations from 18 ppb to under 2 ppb and arsenic from 100 ppb to less than 1 ppb. The process could have broad applications, but would be particularly well-suited for treating wastewater from mining, metals, semiconductor manufacture, as well as groundwater contamination and possibly drinking water.

Prior Research

Ion exchange theory is well established. Typical adsorbents include activated carbon, molecular sieves (which physically trap contaminants), zeolites, carbon molecular sieves, silica gels, activated alumina and clay minerals. Each adsorbent has specific benefits and drawbacks. Some of these adsorbents, in particular the molecular sieves, can be designed to remove specific contaminants. However, many of these are better suited for gaseous waste streams or have had problems with reproducibility.

Research in the past ten years has focused on a variety of measures to improve the performance of ion exchange processes. Cumming et. al. (1997) developed a model to predict the performance of an electrochemical ion exchange. This processes uses electricity to regenerate specially-designed ion exchange resins through polarity reversal.

Lilga et al. (1997) developed an ion exchange system which relied on direct oxidation of an electroactive film attached to an electrode surface. The unique system used a film were composed of nickel hexacyanoferrates deposited on a nickel electrode. During the bench-scale assessment, the researchers proved the ability of the system to remove cesium from concentrated sodium solutions. The researchers, at the Pacific Northwest National Laboratory, applied the system for recovering potassium from pulp and paper mill recovery boilers (Sukamto et. al., 2000).

Neville et al. (1998) used electrochemical ion exchange to remove metals from aqueous streams. This development had a number of specific uses, including removing radioactivity from tank waste storage facilities, recovering precious metals during metal refining operations, and removing base metals from electroplating rinse waters. The authors noted that direct comparison of electrochemical ion exchange to both ion exchange and evaporation showed considerable cost savings.

In an interesting twist, Voortman et. al. (1992) used electrochemical membrane processes to treat aqueous effluent streams. The research team used electrolysis cells incorporating ion-exchange membranes to selectively concentrate, purify and convert various aqueous waste streams. Specific research was conducted in the recovery of sodium hydroxide from textile scour and bottle wash effluents, the removal of sulfuric acid from mine water, and the removal of ammonium nitrate from a nitrogen chemicals manufacturing complex.

Anticipated Costs

Costs associated with selective ion exchange should be fairly modest. EPRI (1996a) estimated the costs of conventional ion exchange system to treat a plating waste (composed of heavy metals, such as chromium) to be approximately $ 200,000 for a 40 gallon per minute waste stream. These costs are highly variable due to the differing nature of the waste stream. Electricity costs associated with ion exchange, however, are quite modest, ranging from 6 to 8 kWh per 1000 gallons treated. The low electric usage of ion exchange is a function of the fact that it is only used in the pumping of the treated liquid. The innovative technology discussed here would use more electricity during the regeneration phase.

AEA Technology (1991) develops data on a variety of treatment technologies. Based on contacting a variety of electroplaters which implemented ion exchange systems to clean plating wastewater, they determined that the net present value of an electrochemical ion exchange system would be similar to a conventional ion exchange plant assuming a cell efficiency of 85 percent and a voltage drop of 15 V, although no actual values were given. These performance characteristics are well within the ability of currently designed electrochemical ion exchange

systems. Current ion exchange media costs range from $ 2.00 to $ 10.00 per pound. The media currently under evaluation in this assessment must be within this range to remain cost effective.

Recommendations to the California Energy Commission

This technology would benefit from continued bench-scale development of specific ion exchange resins to detail the chemistry behind the selective nature of the resin, in order to readily duplicate the performance of this resin, better assess what treatment limitations exist, and properly determine the most appropriate applications. It is possible that the developer of this material has already completed this research and may be resistant to release such information.

Of greater importance is that this should be followed by a demonstration on a suitable industrial wastewater stream. Thus, it is recommended that the CEC fund a demonstration of the technology on an appropriate industrial wastewater stream. This will determine the full-scale feasibility of selective ion exchange. If possible (and additional funding exists), bench-scale research into the chemistry of these specialized resins should also be conducted to more accurately characterize the specialized resins and adsorption kinetics.

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